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Carminite and beudantite from the northern part of the Lake District and from Cornwall.

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Summary. The parageneses are given of ten new occurrences of carminite $[PbFe_2(AsO_4)_2(OH)_2]$ and eleven of beudantite $[PbFe_3AsO_4SO_4(OH)_6]$ in Cornwall and Cumberland, with an account of the alteration of carminite to beudantite and of beudantite to plumbojarosite or to beaverite.

CARMINITE and beudantite are both rare minerals for which very few localities have hitherto been recorded. Hingston Downs Consols mine,[1] Calstock, Cornwall, was for many years the only known British locality for carminite; more recently two further Cornish occurrences, at Wheal Gorland, Gwennap, and at Penberthy Croft mine, St. Hilary, have been recorded,[2] and it is probable that carminite is or has been present at other localities in the West of England. The first recorded British occurrence of beudantite was at Penberthy Croft mine,[3] since when one of us (A. W. G. K.) has found beudantite at some additional Cornish localities: Wheal Gorland; Wheal Carpenter, Gwinear; and Hingston Downs Consols mine. In his account of carminite from this latter mine, Russell mentioned that pharmacosiderite was an associated mineral but that beudantite was not present on his specimens; examination of some scorodite collected near Hitchen's shaft, on the South Lode, by one of us (A. W. G. K.) shortly after the discovery of beudantite at Penberthy Croft mine, has shown minute tufts of brick-red carminite needles accompanied by yellow to yellowish-brown beudantite.

During the last few years we have found that both carminite and

[1] A. Russell, Min. Mag., 1910, vol. 15, p. 255.

[2] A. W. G. Kingsbury, Trans. Roy. Geol. Soc. Cornwall, 1954, vol. 18, part 4 (for 1952), p. 395.

[3] Ibid., p. 392.

beudantite are relatively widespread in the northern part of the Lake District and we have confirmed eight new occurrences of carminite and ten of beudantite. Moreover, our field-work has furnished abundant evidence that carminite is somewhat unstable, and under certain conditions of oxidation or weathering is liable to alter into beudantite. This liability of carminite to alter may well account for its rarity, and for its having been found only in small amounts at nearly all the few recorded localities, except perhaps at Mapimi, Durango, Mexico. At many of these new occurrences, beudantite is unquestionably derived from the alteration of carminite; at others it appears to be of independent formation, but both types show that beudantite itself may undergo further alteration to plumbojarosite or to beaverite, which are closely related species but contain no arsenic.

Where distinctly crystallized, beudantite from Cornwall and Cumberland usually tends to have an acute rhombohedral habit, probably $\{11\bar{1}\}$, as opposed to the more 'cuboid' rhombohedral habit, $\{100\}$, such as is generally shown by the better-known Horhausen and Laurium crystals. This latter habit, which closely resembles that of pharmacosiderite, does, however, occur on some of the Penberthy Croft specimens and also on some specimens from two of the Cumberland localities; at one of the Cumberland localities an unusual hexagonal platy habit has also been found.

Alteration of carminite. It has become clear that much of what was originally carminite, both in Cornwall and in Cumberland, is now represented by pseudomorphs or replacement formations of beudantite; numerous specimens have been found showing this alteration actually in progress, where aggregates of carminite have changed to beudantite on the outside, but still contain an unaltered core of carminite. Since the occurrence of carminite at Wheal Gorland was described, one of us (A. W. G. K.) has collected further specimens at this locality, showing various habits of both carminite and beudantite; some of these, though small, illustrate the alteration in the clearest and most convincing way. In one instance crystalline and crystallized carminite, and yellowish beudantite, were found in a joint in the veinstone, together with green globules; some of the latter had broken across, revealing the radial-fibrous structure and an unaltered core of carminite surrounded by a zone of beudantite. This zone varies slightly in thickness in different globules, but the alteration is here clearly proceeding inwards from the surface; exactly similar radial-fibrous globular aggregates of greenish-brown beudantite have been found at Penberthy Croft mine, but in

most of these the change is almost complete and practically no trace of carminite remains. These aggregates are one of the characteristic habits of carminite. In two other examples, from Wheal Gorland, small acicular crystals of carminite were found to be in the process of altering to beudantite from one end. In many cases, however, the two minerals occur together with no signs of alteration, and appear to have been formed independently.

Alteration of beudantite. At a number of these new localities, particularly in Cumberland, we have found, in addition to well-defined beudantite, other closely similar minerals, which show departures from normal beudantite and which are in various stages of transition to plumbojarosite or beaverite or both. These alterations are clearly seen on many of the specimens, sometimes through the whole sequence

carminite $[PbFe_2(AsO_4)_2(OH)_2] \rightarrow$ beudantite $[PbFe_3AsO_4SO_4(OH)_6]$

$\rightarrow$ plumbojarosite $[PbFe_6(SO_4)_4(OH)_{12}]$

or

carminite $\rightarrow$ beudantite $\rightarrow$ beaverite $[Pb(Cu,Fe,Al)_3(SO_4)_2(OH)_6]$,

with the final elimination of AsO_4. In addition to, and often associated with, these alterations, we have also found well-defined beudantite, plumbojarosite, and beaverite, whose formation appears to have taken place independently; in general, these independent formations appear to have been derived from galena by direct alteration, or perhaps from cerussite, and are usually composed of dense, powdery aggregates without any evidence of derivation from carminite. Nevertheless, some of the plumbojarosite and beaverite and intermediate minerals are clearly the result of further alteration of beudantite.

In the alunite $[A'B'''_3(SO_4)_2(OH)_6]$ and beudantite $[A''B'''_3(As,P)O_4 SO_4(OH)_6]$ groups, both the A and B cation positions, and particularly the former, appear to be very tolerant as regards ionic size.[1] There may be a range of substitution in the A position as is shown, for example, between jarosite and natrojarosite, and a more limited substitution in the B position as is shown between alunite and jarosite; a considerable range of compositional variation is also shown by some members of the isostructural plumbogummite $[A''B'''_3((P,As)O_4)_2(OH)_5 \cdot H_2O]$ group. In the beudantite group, according to the limited amount of published data available, there is also some substitution among the anions (for example, of AsO_4 for PO_4 in corkite, the phosphate analogue of beudantite), while

[1] Dana, Syst. Min., 7th edn, vol. 2, p. 556.

some analyses of other phosphate members of the group show a departure from the 1:1 ratio between SO_4 and PO_4. The analysis and designation as 'beudantite–plumbojarosite', however, of the mineral from the Belvedere gold mine, Mount McGrath, Western Australia,[1] not only shows a gradation towards the jarosite group and a departure from the normal 1:1 ratio of AsO_4 to SO_4, with a decrease of AsO_4 and PbO and an increase of SO_4 and Fe_2O_3, but suggests that this particular mineral falls within the alteration-series mentioned above in connexion with the Cornish and Lake District occurrences. Very few occurrences of beudantite have so far been recorded; Dana[2] mentions the Mount McGrath occurrence and three others, and Guillemin[3] has recently recorded beudantite with carminite from Cap Garonne, Var, France. This paucity of recorded occurrences would account for the lack of data on variations in the cation and particularly the anion ratios. With the exception of the Western Australian occurrence, and those in Cornwall and the Lake District, the presence of beudantite does not appear to have been recorded with any of the other numerous occurrences of plumbojarosite and beaverite, so that the alteration-sequences referred to above have not been observed.

It may be that local oxidation conditions in the veins in Cornwall and in the Lake District, largely as the result of their mineral assemblages, gave rise to these particular alterations. In this connexion it is to be noted that in all these Cornish and Lake District occurrences, arsenopyrite is present in the veins as well as other-sulphides of iron, copper, lead, and zinc.

Because of the small amount of available material, often closely associated with other minerals, identification has been carried out mainly by X-ray study. Using cameras of 9-cm., 11·46-cm., and 19-cm. diameter, powder-photographs of a large number of samples have enabled specimens of beudantite, plumbojarosite, and beaverite to be distinguished clearly, not only from each other but from other minerals in the alteration series. Almost pure beudantite crystals from Laurium in Greece have furnished our standard photographs of this mineral. Samples of analysed plumbojarosite from the Tintic Standard mine, Utah, and from other well-known American localities, have been generously supplied by Dr. W. T. Schaller, of the U.S. Geological Survey, and also by Professor Horace Winchell, from the Brush Collection at the

[1] E. S. Simpson, Journ. Roy. Soc. Western Australia, 1938, vol. 240, p. 110.
[2] Syst. Min., 7th edn, vol. 2, p. 1002.
[3] Bull. Soc. Franç. Min. Crist., 1952, vol. 75, p. 70 [M.A. 12–68].

University of Yale; Dr. Schaller also supplied a sample of beaverite from his analysed type-material,[1] and we thank him and Professor Winchell for their help and generosity. From the large number of powder-photographs obtained it has been possible to see if and where specimens of the various Lake District and Cornish minerals were intermediate between beudantite and plumbojarosite or beaverite; in a number of cases it was evident that the specimens were mixtures. Among the intermediate minerals many of the patterns and spacings showed the characteristics of both beudantite and one of the other two species (indicating a probable half-way alteration); others again showed probable compositional variations or almost complete alteration. While chemical analyses in conjunction with the X-ray studies would obviously have been desirable, had they been practicable, the results obtained have nevertheless indicated clearly the processes that appear to have been taking place.

New occurrences of carminite and beudantite. As carminite and beudantite, as well as other minerals in the alteration series referred to above, occur together at many of the new localities found, both in the Lake District and in Cornwall, it is convenient to list them under the localities with a description of their associations.[2]

Lake District, Cumberland.

Grains Gill, Carrock Fell. Beudantite has been found here as brown, powdery aggregates in gossany material from near the intersection of an east–west 'lead-vein' with the north–south Emerson vein of the 'granitic' suite. Associated minerals fall within the alteration series referred to above, but carminite appears to be absent from this locality.

Higher part of Brandy Gill, Carrock Fell. About three-quarters of the way up the gill, an east–west Cu–Pb–As vein, in altered granophyre, outcrops on the west side. This vein intersects, and in each case displaces to the left, a number of north–south veins and strings, which form the northern extremities of the more westerly members of the 'granitic' suite of veins in Grains Gill[3] half a mile to the south. These 'granitic' veins and strings in the higher part of Brandy Gill, as well as the adjacent country-rock, contain much arsenopyrite; oxidation of this, or reaction

[1] Butler and Schaller, Journ. Wash. Ac. Sci., 1911, vol. 1, p. 26; Amer. Journ. Sci., 1911, ser. 4, vol. 32, p. 418.

[2] See also A. W. G. Kingsbury and J. Hartley, Min. Mag., 1956, vol. 31, p. 289, and 1957, vol. 31, p. 700.

[3] In Grains Gill several east–west 'lead-veins' also heave and shift to the left the main 'granite' veins; later quartz–carbonate veins cross and heave them to the right.

with the mineralizing solutions and minerals of the east–west vein, has produced a great variety of secondary arsenates. Carminite must formerly have been abundant and, though not rare, most of it has now altered to beudantite. Small unaltered patches of carminite are fairly widely distributed through and on the altered granophyre walls of the vein; on the cheeks of the vein it is associated with large amounts of beudantite, which forms crystalline coatings and crusts, yellow, yellow-green, greenish-brown, and brown in colour, most of which are pseudomorphous after or derived from alteration of carminite. In one instance a hollow hexagonal epimorph was found (probably after mimetite) of which one end consisted of carminite, the middle portion of beudantite, and the other end of beaverite. At the intersections with the east–west vein, which were examined *in situ*, the north–south strings are themselves impregnated with carminite for several inches on either side of the east–west vein. Most of the carminite shows the characteristic deep carmine-red colour, and usually forms drusy botryoidal or crystalline aggregates and crusts: it has also been found in cavities in the vein, where it is usually associated with beaverite (some of which has formed directly from and is pseudomorphous after galena), mimetite, and bayldonite, and occasionally it occurs in minute prismatic crystals.

In addition to its widespread occurrence in the wall-rock, beudantite has been found well crystallized in quartz in the vein, both as aggregates of small brown acute rhombohedra, and as small (up to 2 mm.), brown, partly zoned hexagonal plates: the latter show a large basal plane and narrow faces of two rhombohedra or of the hexagonal prism or of all three, and this appears to be the first recorded occurrence of this euhedral platy habit. A little carminite is associated with beudantite of both habits.

Dry Gill mine, Caldbeck Fells. Beudantite has been found here, in material from the middle cross-cut about half-way up the gill, as greenish-yellow powdery aggregates associated with olivenite, and in material from the lower day-level[1] as yellow crystalline and brown fine-grained aggregates, with baryte, azurite, and 'psilomelane'. Some of this material appears to be derived from carminite, although no traces of the latter have yet been found.

Driggith mine, Caldbeck Fells. Carminite occurs in very small patches, associated with yellowish-brown microcrystalline beudantite, mimetite, and cerussite, an iron-stained granular quartz from the outcrop of the main vein. Beudantite also occurs in yellow-brown to brown powdery

[1] Driven alongside the vein where it outcrops and crosses the Dry Gill beck.

aggregates investing decomposing galena and cerussite from the outcrop of the vein; some of this beudantite falls within the alteration-series mentioned above (p. 425).

Netherrow Brow, Caldbeck. (*a*) In iron-stained spongy quartz vein-stone derived from an old cross-cut between Sandbed mine and Pottsgill barytes mine, driven to the near-outcrop of a north-west–south-east vein, carminite occurs as small residual patches with considerable amounts of yellow-green, yellow-brown, and brown earthy and micro-crystalline beudantite, together with red-brown scorodite, beaverite, and 'limonitic' matter. (*b*) In material from an old level, near the farm of Nether Row, driven on the same vein as the preceding and about 800 yards to the north-west, carminite occurs in small drusy globular aggregates, associated with small yellow acute rhombohedra of beudantite, brown scorodite, and minute tufts of arseniosiderite. Beudantite also occurs in considerable amounts as compact yellow, yellow-brown, green-brown, and brown powdery and micro-crystalline aggregates associated with yellow mimetite, mottramite, green and brown scorodite, pharmacosiderite, and yellowish and yellowish-brown powdery plumbojarosite and beaverite. A few 'cuboid' rhombohedra of beudantite have been found on some specimens. The unaltered vein material carries fine-grained and disseminated arsenopyrite, pyrite, galena, some blende, and traces of chalcopyrite.

Pottsgill barytes mine, Caldbeck. At the head of the Gill Beck a small copper vein, apparently north-north-west–south-south-east, was cut by the old No. 1 cross-cut of the barytes mine and much material from it lies on a small dump near the entrance to the cross-cut. The vein apparently contained mainly chalcopyrite, together with galena, blende, and arsenopyrite or other arsenic-bearing minerals. There are also in the vicinity a number of small veins and strings carrying galena, pyrite, arsenopyrite, and some löllingite, some of which may also have been cut by the cross-cut. Among the material derived from the copper-vein, carminite has been found in tufts of minute, brick-red, tapering acicular crystals associated with acute rhombohedra of yellow-brown beudantite, scorodite, and pharmacosiderite, in a gossany quartz–goethite matrix. Beudantite also occurs as a powdery yellow to yellow-brown coating on altering galena.

Ingray Gill, Caldbeck (*between Haygill and the hamlet of Fellside*). An unrecorded north-north-west vein crosses the head of the gill and has two cross-cuts on it; the whole area is covered with drift, and no signs of the vein outcrop are visible. In material from the northern cross-cut, a little

carminite is present as tufts of minute prisms in cavities in saccharoidal quartz, associated with beudantite in minute yellow rhombohedra, scorodite, and pharmacosiderite. Beudantite is also present, forming yellowish-brown powdery and crystalline coatings on decomposing galena and quartz.

Higher Roughton Gill, Caldbeck Fells. Carminite has been found in the outcrop of the main south vein, along the south-eastern flank of Balliway Rigg, forming drusy botryoidal aggregates and tufts of minute prisms in cavities in quartz, with yellow rhombohedra of beudantite, some of them attached to the surface of the carminite, and small, colourless, tapering prisms of mimetite. Beudantite has also been found here as yellowish-brown, greenish-brown, and brown powdery and crystalline aggregates associated with decomposing galena, cerussite, chrysocolla, jarosite, and plumbojarosite, and minerals in the alteration-series beudantite to plumbojarosite and beudantite to beaverite.

Wanthwaite mine, St. John-in-the-Vale, near Threlkeld. Two veins were worked at this little-known mine: (*a*) The southern vein, occupying the faulted junction between Skiddaw Slates and the Borrowdale Volcanic Series, under Wanthwaite Crags, is mainly a fault-breccia of smashed slate cemented by quartz, carbonates, and various sulphides; it also contains, on the hanging-wall, a thick rib of quartz impregnated with a massive granular intergrowth of arsenopyrite, pyrite, galena, blende, and, rarely, traces of chalcopyrite. At the outcrop, *in situ* on the hanging-wall, this rib has oxidized to iron-stained skeletal quartz, cavities in which now contain small residual patches of carminite, with large amounts of yellow, yellowish-green, buff, and brown beudantite, some of it powdery and some minutely crystallized, with scorodite, both green and reddish-brown, and pharmacosiderite. Traces of 'cuboid' rhombohedra of beudantite, largely altered, also occur here. (*b*) The northern vein, in the (probably) faulted boundary between the Skiddaw Slates and the Threlkeld microgranite, on Wanthwaite Bank and up to Clough Head, contains similar primary minerals but in smaller amounts. Yellow-brown beudantite, part powdery and part micro-crystalline, occurs together with minerals in the beudantite → plumbojarosite alteration-series on decomposing galena from a lower level on the vein on Wanthwaite Bank.

New localities for beudantite in Cornwall.

Wheal Gorland, Gwennap. Beudantite here occurs as minute, yellow rhombohedra on the surface of drusy botryoidal carminite; also as yellow,

yellowish-green, and green drusy crystalline crusts, and green globular aggregates, associated with and partly pseudomorphous after carminite, in joints in a pink quartz matrix; it is also closely associated with zeunerite[1] and mimetite.

Wheal Carpenter, Gwinear. Beudantite here occurs as yellowish-green to greenish-brown crystalline crusts associated with bayldonite, on quartz. Small amounts of carminite also occur, in such a manner as to suggest that the beudantite has formed at its expense.

Specimens collected more recently at Penberthy Croft mine, St. Hilary, show beudantite in crusts, globular aggregates after carminite, and 'cuboid' rhombohedra, with a remarkable range of colour through various shades of yellow, green, and brown to almost black; some of these specimens also show small residual patches of carminite. Further examples of intermediate beudantite → beaverite and beudantite → plumbojarosite have also been found.

Although the carminite from all these localities, both in the Lake District and in Cornwall, has a characteristic appearance and is in most cases readily recognizable in the field, all the occurrences have been verified by X-ray and other methods, and powder-photographs have all shown agreement with those of carminite from Mapimi and from previously confirmed Cornish occurrences.[2]

Note: Since this paper was originally prepared, one of us (A. W. G. K.) has found three more localities in Cornwall for carminite and beudantite:

Treore mine, St. Teath. This locality lies immediately south of Treore farm, about $1\frac{3}{4}$ miles east-south-east of Port Isaac. The vein, trending north-north-east, was at one time worked for arsenic, being rich in arsenopyrite and pyrite in a gangue of brecciated slate and quartz, chalybite, and ankeritic carbonates. Associated ore minerals are galena, chalcopyrite, blende, stibnite, jamesonite, and other antimony-bearing sulphides. The principal secondary minerals are mimetite and scorodite, carminite and beudantite occurring in association with these. One specimen is of particular interest in that it shows two alteration-sequences:

[1] A. W. G. Kingsbury, Trans. Roy. Geol. Soc. Cornwall, vol. 18, part 4 (1952), p. 396. A sample of this material, examined shortly after collection, was shown to be zeunerite, with n 1·608 ± 0·001 and giving X-ray powder-pattern spacings almost identical with those for synthetic hydrous zeunerite given by J. Weiss-Frondel in Amer. Min., 1951, vol. 36, p. 252, and distinct from those of meta-zeunerite with 5–8 H_2O.

[2] Representative specimens of most of the above occurrences have been given to the Department of Mineralogy, British Museum (Natural History).

in one, crystals of mimetite have been partially or completely replaced by pseudomorphs of carminite, which in turn has partially or completely altered to beudantite; in the other sequence, larger areas of green beudantite are accompanied by patches of residual carminite, some of which are coated with yellow rhombohedra of beudantite of later formation, and some patches of the green beudantite are sprinkled with a second generation of mimetite crystals.

Old Treburgett mine, St. Teath. This mine lies about $2\frac{1}{4}$ miles east by south of Treore mine, and $\frac{3}{4}$ mile south-west of St. Teath village, on the northern part of a north-east vein and an associated cross-course. A gangue of brecciated country-rock and quartz, with calcite, ankerite, and chalybite, carried galena and blende as the principal ore minerals, with minor arsenopyrite and some antimony-bearing sulphides. Carminite occurs in cavities in decomposing arsenopyrite as drusy botryoidal aggregates, together with a little yellow beudantite, scorodite, and traces of mimetite. Very little alteration of the carminite has taken place at this locality.

Pengenna (Trewethen) mine, St. Kew. This locality lies about $\frac{3}{4}$ mile south-west of Old Treburgett mine, on the southern part of the same vein (here known as the Trewethen lode) and on another vein (the Pengenna lode) trending nearly due north. The latter vein carried some antimony minerals in the upper part, but mainly galena in depth. Both carminite and yellowish beudantite are present in the oxidized vein-material, associated with mimetite and scorodite.

X-ray data on stokesite.

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[Taken as read 31 March 1960.]

Summary. An X-ray examination of the type specimen of stokesite gave a 14·41, b 11·61, c 5·23 Å.; space-group *Pnna*. The unit cell contains 4[$CaSnSi_3O_{11}H_4$] and is derived from Hutchinson's morphological unit by the transformation [010/001/100]. X-ray powder data are given.

STOKESITE, a tin-bearing silicate, occurs on a matrix of axinite from Roscommon Cliff, St. Just, Cornwall. The transparent well-crystallized mineral resembles selenite, but a careful examination by Hutchinson (1899, 1900) established it as a new mineral species. Goniometric and optical measurements, together with micro-chemical analyses, were carried out, and these showed that the mineral belonged to the orthorhombic holosymmetric class ($a:b:c$ = 0·3463:1:0·8033) and that an empirical formula $CaSnSi_3O_{11}H_4$ was probable. Since that time no further occurrence has been described, and the original crystal and fragments in the Museum of the Department of Mineralogy and Petrology, Cambridge, remain the only known example of this mineral. X-ray data for this material are reported in this paper.

A small fragment obtained from a thick section in the museum collection was examined by oscillation and Weissenberg methods using Cu-$K\alpha$ radiation. The diffraction patterns confirmed the orthorhombic symmetry, with cell dimensions a 14·41, b 11·61, c 5·23 Å. (all $\pm$0·03), and the systematic absences showed that the space-group is *Pnna*. Powder photographs of material from the same section were taken with Cu-$K\alpha$ radiation. The observed spacings are given in table I, together with the spacings for the first eighteen lines calculated from the cell dimensions; there is good agreement between the observed and calculated values. The three strongest lines are at 3·99, 2·89, 7·25 Å., though the line at 2·89 Å. is obviously a doublet at least.

From an examination of the X-ray data it is apparent that although the correct parametral plane was chosen in the morphological description,

TABLE I. Powder data for stokesite.

$d_{obs.}$	$I.$	$hkl.$	$d_{calc.}$	$d_{obs.}$	$I.$	$d_{obs.}$	$I.$
7·25	s	200	7·21	2·23	m	1·534	vw
5·82	m	020	5·81	2·15	m	1·521	vw
4·95	vw	101	4·92	2·12	m	1·511	m
4·79	w	011	4·77	2·04	m	1·486	m
4·54	m	111	4·53	1·992	vw	1·451	w(b)
		220	4.52	1·938	w	1·440	vw
3·99	vs	211	3·98	1·906	w	1·427	w(b)
3·76	w	121	3·75	1·877	vw	1·384	m
3·55	m	301	3·54	1·832	m	1·370	vvw
3·43	m	410	3·44	1·808	w	1·322	m
		221	3·42	1·774	m	1·309	w
3·03	m	131	3·04	1·755	vw	1·302	w
2·89	vs(b)	400	2·90	1·726	w	1·253	vw
		411	2·87	1·711	m	1·235	vw
		231	2·86	1·694	vw	1·194	vvw(b)
2·69	m	240	2·69	1·678	m	1·178	vvw(b)
2·65	vw	421	2·64	1·593	w	1·141	vw
		430	2·64	1·556	ms	1·128	w
2·62	w	002	2·62	1·545	vw	1·125	w
		331	2·61				
2·52	vw	501	2·52				
2·47	vw	511	2·47				
2·39	m	241	2·39				
		022	2·38				
2·36	vw	122	2·36				
		431	2·36				
		610	2·35				
2·27	m	222	2·26				
		440	2·26				

the morphological axes would not lead to the conventional space-group symbol; the relationship between the old morphological axes and those chosen in this study is $a_m = c_x$, $b_m = a_x$, $c_m = b_x$. If the axial ratio obtained from the cell dimensions is transformed to correspond with the original morphological orientation, a value $a:b:c = 0{\cdot}3627:1:0{\cdot}8056$ is obtained, in satisfactory agreement with Hutchinson's determination. The original morphological and optical data may also be described in terms of the new axial orientation: dominant forms {100} and {211}, with perfect {101} cleavage and imperfect {100} cleavage; α (1·609) $\parallel c$ [001], β (1·6125) $\parallel a$ [100], γ (1·619) $\parallel b$ [010], $2\,V_\gamma = 69\frac{1}{2}°$ for Na light).

Analyses on two portions of 100 mg. each gave Hutchinson 43·1 % SiO_2, 33·3 % SnO_2, 13·45 % CaO, 8·6 % H_2O. Using these figures, and the density of 3·185, the contents of the unit cell are $Ca_4Sn_{3\cdot8}Si_{12\cdot3}O_{44\cdot4}H_{16\cdot3}$, which suggests the idealized formula $CaSnSi_3O_{11}H_4$ (identical

with that proposed by Hutchinson) with $Z = 4$. With the small amount of mineral available it was not possible to make any further chemical determination. Dr. J. V. P. Long kindly determined the calcium and tin contents by the X-ray emission micro-analytical technique (Castaing, 1951); his results of $13{\cdot}3 \pm 0{\cdot}6$ % CaO and $33{\cdot}7 \pm 1{\cdot}9$ % SnO_2 confirm, within the experimental error, the original analysis.

Hutchinson suggested that stokesite had a formal resemblance to catapleiite ($Na_2ZrSi_3O_{11}H_4$). However, powder photographs of stokesite show little resemblance to those of catapleiite, which has trigonal symmetry. Further it has been found that catapleiite contains three-membered $(SiO_3)_3$ rings like benitoite (Belov, 1942); the 5·23 Å. *c*-axis of stokesite suggests that the Si–O tetrahedral arrangement is more closely related to the normal band or sheet silicate structures. Such speculations can only be resolved by a detailed structure determination, which should not be an intractable problem owing to the presence of the heavy tin atoms in special positions; it is hoped that a structure determination will be carried out at a later date.

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The kinetics of the ordering process in triclinic $NaAlSi_3O_8$

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Summary. A kinetic analysis is presented of the data of MacKenzie (1957) on the hydrothermal treatment of $NaAlSi_3O_8$ under isobaric, isothermal conditions in the temperature range 450° C. to 1000° C.

The analysis indicates the existence of a smeared polymorphic transformation in the temperature range around 600° C. The activation energy for the transformation is about 60 kcal. mole^{-1} and has been equated with the process of self-diffusion involved in Al–Si ordering in the structure. Some dry-heating experiments and the influence of varying water vapour pressure are discussed.

IT is our purpose to present a kinetic analysis of the experimental data of MacKenzie (1957) on the thermal transformation in triclinic $NaAlSi_3O_8$.[1] The advantages of studying MacKenzie's data on the transformation in triclinic $NaAlSi_3O_8$ in kinetic terms may be summarized briefly as follows. In studying equilibration rates in this way due allowance can be made for the temperature dependence of the rates and it is possible to demonstrate any singular changes or discontinuities in rate that are associated with change in equilibrium structural state as a function of temperature. Choice of an appropriate rate law permits one to extrapolate from incomplete equilibration data to the equilibrium state, but this is of secondary importance in an analysis of this type.

Kinetic data can only provide information about an accessible equilibrium state. The latter may be defined as an equilibrium state towards which a measurable rate of approach can be observed. Kinetic data taken by themselves do not define the status of an equilibrium state. A system may be defined as *quasi-equilibrated* if, under a given set of physico-chemical conditions, it does not move towards the true equilibrium state in any finite time. Such a state corresponds to a free energy minimum other than the lowest one appropriate to the imposed conditions, and results if the free energy of activation for passage to the true equilibrium state is prohibitively large.

[1] It is considered advisable to restrict the use of the mineral name 'albite' to naturally occurring material since triclinic $NaAlSi_3O_8$ prepared in hydrothermal experiments may not be identical in every respect with natural albites.

Classification of polymorphic transformations. In order to facilitate later discussion of the character of the transformation in triclinic $NaAlSi_3O_8$, as defined by the kinetic data, it is necessary to comment here on some general aspects of polymorphic transformations. An important and practical classification of these is due to Ubbelohde, who emphasized, in an important review in 1957, that the thermodynamics of transformation in the solid cannot always be considered from the purely classical viewpoint, since co-operative effects in the solid must be considered.

Ubbelohde defined as *discontinuous* those transformations that show classical discontinuity in the measured specific heat and molar volume as functions of pressure and temperature. In practice such transformations usually involve major structural reorganization. *Continuous* transformations he defined as those that show no such discontinuity. Where continuity can be associated with the stable coexistence of two or more closely related structural modifications over a range of temperature, Ubbelohde has applied the term *smeared*. In the temperature range of a smeared transformation the free energy must include terms arising from the strain and internal surface energy associated with domain boundaries.

The domain texture produced under such conditions may render the true equilibrium state of the system inaccessible at lower temperatures because of the improbability of the necessary thermal fluctuations. In terms of the definition presented earlier such a system would be described as quasi-equilibrated at the lower temperature (cf. Bragg, 1940, for a discussion of similar effects in alloys).

Kinetic methods of detecting and studying polymorphic transformations. A number of techniques that utilize the theory of rate processes have been applied to the study of polymorphic transformations in solids. Examples include the use of electrical conductivity measurements by Landon and Ubbelohde (1957) and the use of isothermal diffusion coefficients by Johnson, Bristow, and Blau (1951). In such experiments, since the rate-controlling mechanism is one of diffusion, the temperature dependence of the rate processes may be described by the Arrhenius relationship $k = Ae^{-E_a/RT}$, where k is a suitably defined rate constant, E_a is the activation energy for the rate-controlling step in the diffusion process and is usually stated in calories/mole, T is the absolute temperature, R the gas constant, and A a term that includes the entropy of activation. In the temperature range of a thermal transformation A may change in value owing to the change in mechanism of the diffusion

process. Outside such a temperature range A should be relatively independent of temperature.

The Arrhenius relationship may be applied to any rate process in which the rate-controlling step is one of diffusion. If a thermal transformation involves self-diffusion the application of this relationship to isothermal, isobaric equilibration rates from a defined initial structural

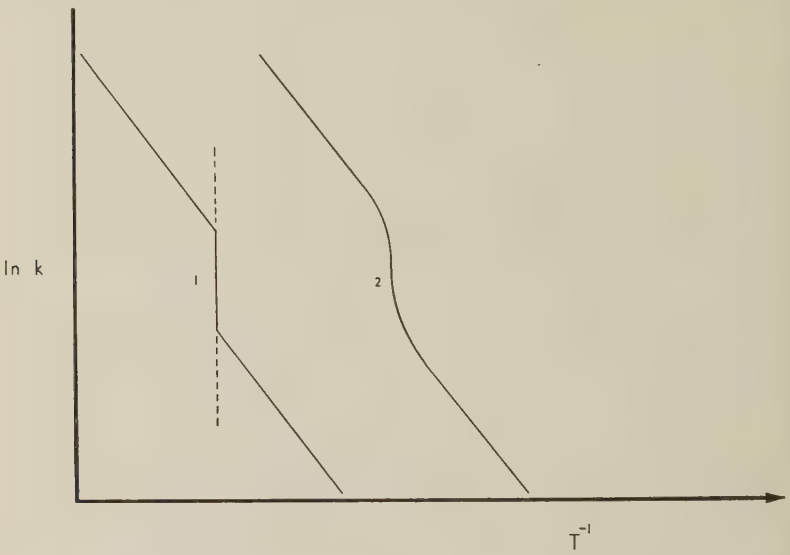

FIG. 1. Hypothetical Arrhenius plots of discontinuous (1) and continuous (2) transformations.

state is valid. The diffusion potential, in this case, is defined by the free energy difference, ΔG, between the initial and equilibrium structural states at the temperature concerned and the character of the Arrhenius plot may be used to interpret the nature of the change in accessible equilibrium state as a function of temperature. If a structural transformation of appreciable magnitude occurs in the temperature range studied this will define, in general, a change in the A term of the Arrhenius relationship. An appropriate Arrhenius plot should demonstrate such a change; it may also provide direct evidence on the continuity and character of the transformation involved.

To illustrate this point schematic Arrhenius plots for a discontinuous and continuous transformation have been presented in fig. 1.

In attempting kinetic analysis of the isobaric, isothermal equi-

libration data presented by MacKenzie for the transformation in triclinic $NaAlSi_3O_8$ it is convenient, in the first instance, to use a relationship of the form $k = |\Delta G| A e^{-E_a/RT}$. The validity of this relationship can best be tested by studying the corresponding plot of ln k as a function of T^{-1} for the observed equilibration rates.

Experimental data.

In his main series of experiments MacKenzie (1957) was concerned with the behaviour under isothermal, isobaric conditions of a glass of composition $NaAlSi_3O_8$. The experiments cover the temperature range 450° C. to 1 000° C., and were mostly performed at p_{H_2O} 14 000 lb./in.^{2} He observed that crystallization to triclinic $NaAlSi_3O_8$ occurs rapidly and is followed by a slow change in unit cell dimensions. The post-crystallization changes in charges held for various times at known constant temperature and p_{H_2O} were followed by measurement after quenching of $2\theta_{131}-2\theta_{1\bar{3}1}$ on diffractometer traces taken with Cu-$K\alpha$ radiation. The variable $2\theta_{131}-2\theta_{1\bar{3}1}$ may be defined as obliquity and designated ψ. Obliquity-time data are given in full in table 3 (pp. 490–492) of MacKenzie (1957) and need not be reproduced here. Some further data were made available to us by Dr. W. S. MacKenzie, and are set down, with permission, in our table I.

Table I. Values of $\psi = 2\theta_{131}-2\theta_{1\bar{3}1}$ for $NaAlSi_3O_8$ crystallized for different lengths of time. (We are indebted to Dr. W. S. MacKenzie for permitting us to include these unpublished additional data.) In all runs p_{H_2O} was 14 000 lb./in.^{2}

Run no.	Time (hours)	ψ	Run no.	Time (hours)	ψ
525° C.			550° C.		
336	71	1·826	88	24	1·900
351	71	1·816	357	71	1·832
350	232	1·789	338	71	1·814
335	327	1·774	315	140	1·772
			356	232	1·799
550° C.			314	258	1·722
287	24	1·833	337	327	1·816
288	24	1·835			
87	24	1·895			

MacKenzie also performed some subsidiary hydrothermal experiments and dry-heating experiments, which will be discussed later (p. 448). Only the data for the main series of experiments are involved in the sections immediately following.

The usefulness of the obliquity parameter ψ for following the change

from the initially crystallized structure towards the equilibrium structure at any temperature and p_{H_2O} could not be evaluated *a priori*, since ψ has no clear quantitative relationship to structural state. The use, however, of rate constants derived from ψ is analogous to the use of electrical conductivity by Landon and Ubbelohde (1957) and of diffusion coefficients by Johnson, Bristow, and Blau (1951) in the study of thermal transformations in Na_3AlF_6 and sodium silicate glasses respectively.

Kinetic analysis of mackenzie's main series of experiments.

The rate law. The rate of approach to equilibrium at any time is likely to be dependent in some simple manner on the amount of the departure of the system from equilibrium at that time. In terms of obliquity departure from equilibrium is measured by $\psi-\psi_\infty$, where ψ_∞ is the value towards which the obliquity tends at infinite time. Of simple rate laws based on $(\psi-\psi_\infty)^n$ it was found that the experimental data fitted best a law of the form

$$-d\psi/dt = k(\psi-\psi_\infty)^2. \quad (1)$$

The rate constant k is, to a first approximation, a function of temperature and p_{H_2O} only.

On integration and insertion of the limit $\psi \to \psi_0$ as $t \to 0$, the rate law becomes

$$kt = (\psi_0-\psi)/(\psi-\psi_\infty)(\psi_0-\psi_\infty). \quad (2)$$

The limiting obliquity ψ_0 is the extrapolated starting value of ψ, the value ψ would have had at zero time if the glassy charge had crystallized instantaneously instead of in half an hour or so. No physical meaning is attached to the value of ψ_0.

The integrated rate law is most conveniently represented in logarithmic form, as

$$\log(\psi_0-\psi)/(\psi-\psi_\infty) = \log t+\log k(\psi_0-\psi_\infty). \quad (3)$$

Fig. 2 shows a plot of $\log(\psi_0-\psi)/(\psi-\psi_\infty)$ against $\log t$ of the data for 700° C., p_{H_2O} 28 000 lb./in.^{2}

Evaluation of limits. The experimental data are such that accurate values of ψ_0 and ψ_∞ cannot usually be obtained by inspection. However, by rearranging the rate law in the form

$$\psi = \psi_0-k(\psi_0-\psi_\infty)(\psi-\psi_\infty)t, \quad (4)$$

estimating ψ_∞ by inspection, and plotting ψ against $(\psi-\psi_\infty)t$, an accurate value of ψ_0 can be obtained from the intercept on the ψ-axis. The value

of ψ_∞ may then be refined by inserting the new value of ψ_0 in the rate equation written in the form

$$\psi = \psi_\infty + \{(\psi_0 - \psi)/t\} \cdot \{1/k(\psi_0 - \psi_\infty)\}, \tag{5}$$

plotting ψ against $(\psi_0 - \psi)/t$, and determining ψ_∞ from the intercept on

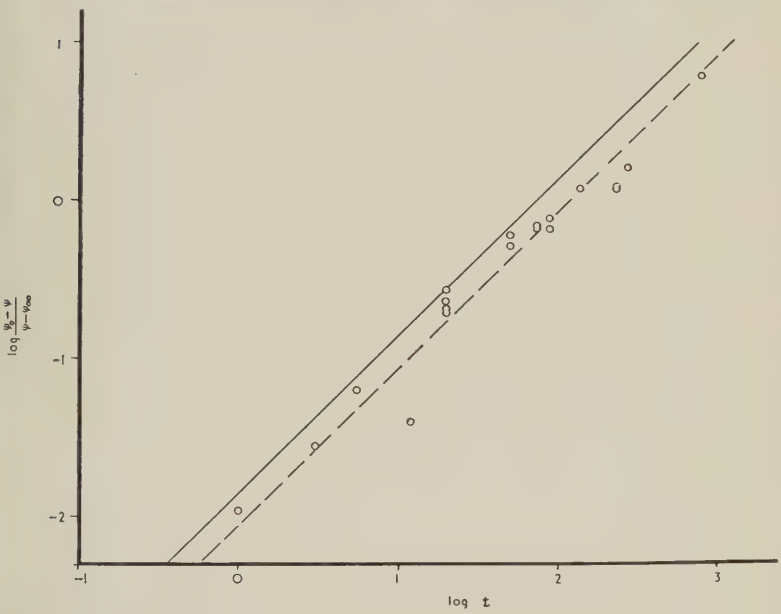

FIG. 2. Logarithmic plot of $(\psi_0 - \psi)/(\psi - \psi_\infty) = k(\psi_0 - \psi_\infty)t$ for 700° C., p_{H_2O} 28 000 lb./in.^{2} The solid line corresponds to k^*, and the broken line to $\bar{k}$.

the ψ-axis. Further refinement of ψ_0 can be achieved by replotting equation (4) using the improved value of ψ_∞ obtained from (5). Further refinement of ψ_∞ can then be achieved by replotting (5) using the improved value of ψ_0. The refinement procedure was repeated successively for ψ_0 and ψ_∞ until no further significant change occurred. Final values of ψ_0 and ψ_∞ are given in table II.

The value of ψ_∞ could not be estimated by inspection of the data for the lowest temperatures. For the first stage in the refinement, therefore, values were chosen consistent with the known variation of ψ_∞ with temperature at higher temperatures.

The limits ψ_0 and ψ_∞ are functions of temperature and of p_{H_2O}. Their dependence on p_{H_2O} will be considered in a later section (p. 446). The variation of ψ_∞ with temperature is shown in fig. 3, which differs from

TABLE II. Final estimates of the limiting obliquities ψ_0 and ψ_∞.

T (°C.)	p_{H_2O} (lb./in.²)	ψ_0	ψ_∞	T (°C.)	p_{H_2O} (lb./in.²)	ψ_0	ψ_∞
1 000	2 000	2·025	2·005	550	14 000	1·935	1·600
900	7 000	2·002	1·970	525	14 000	1·930	1·475
850	14 000	1·995	1·940	525	7 000	1·930	1·495
800	14 000	1·985	1·905	500	14 000	1·925	1·275
750	14 000	1·973	1·870	475	14 000	1·920	1·15
700	28 000	1·966	1·782	450	14 000	1·918	1·10
600	14 000	1·950	1·704				

the corresponding plot in MacKenzie (1957, p. 508) in being smoother due to the refinement of ψ_∞, and in extending to lower temperatures where an obvious turnover towards the obliquity of low albite is discernible. Fig. 3 thus represents the temperature dependence of structural state, as measured by obliquity, for triclinic $NaAlSi_3O_8$ equilibrated or quasi-equilibrated under MacKenzie's experimental conditions. Although it would probably be incorrect to interpret the structural states of soda-feldspars equilibrated under natural conditions quantitatively in terms of fig. 3, a semi-quantitative correspondence may be expected.

The obliquities of high albite (1·99) and of low albite (1·062) inserted on fig. 3 are those of Smith (1956), whose value for high albite differs from that (2·03) of Tuttle and Bowen (1950).

Determination of rate-constants. Rate-constants were calculated for each experimental point using equation (3) above. The scatter of the experimental points beneath the line of fastest rate, apparent in fig. 2, greatly exceeds the scatter attributable to error in the measurement of ψ ($\pm$0·004). The increased scatter must represent some real difference in the experimental conditions between individual experiments, and MacKenzie (1957, p. 499) considered in this connexion the influence of grain size. The most significant experimental points are those corresponding to the fastest rates; only the rate-constants, designated k^*, calculated from such points are used in subsequent sections. Values of $\log k^*$ are given in table III.

The rate-constants are pressure-dependent. Values of $\log k^*$ derived from experiments at various pressures, corrected to p_{H_2O} 14 000 lb./in.² by the method of p. 446 where necessary, are also given in table III and plotted against $1/T$ in fig. 4.

An average rate-constant $\bar{k}$ has also been calculated, using equation (3), from all the experimental points under each set of physical conditions. Values of $\log \bar{k}$ with standard deviation and corrected to p_{H_2O} 14 000

lb./in.^{2} where necessary are given in the last column of table III, and plotted against $1/T$ in fig. 4.

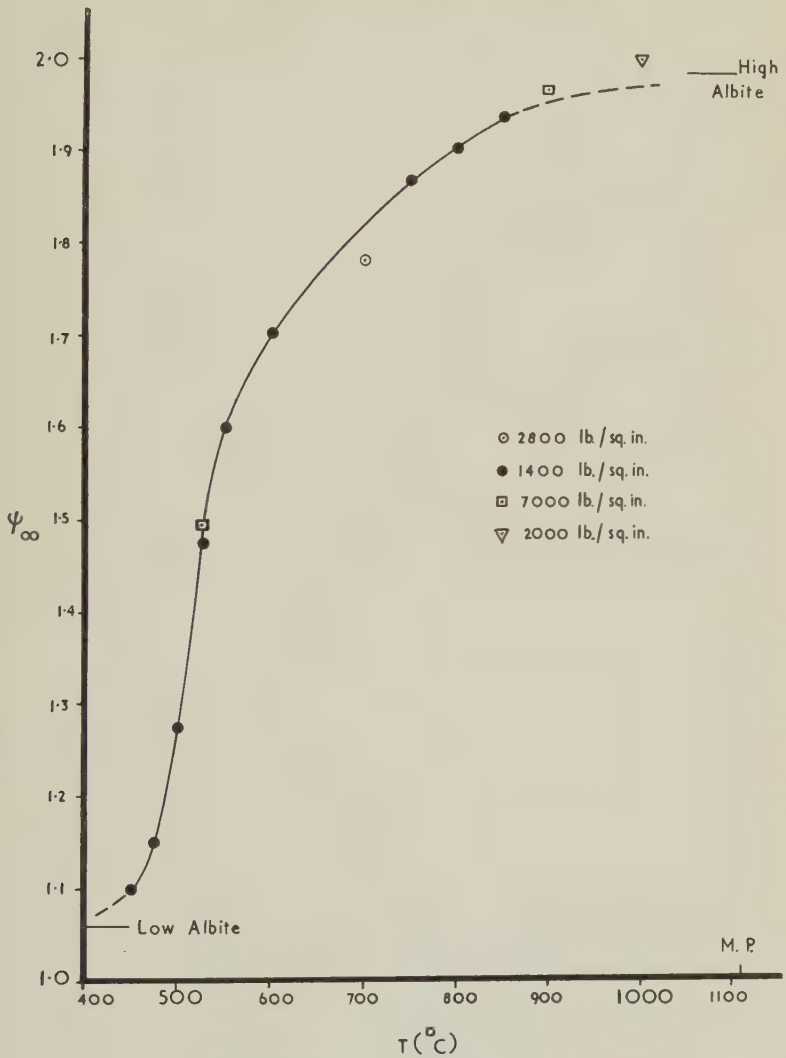

Fig. 3. The temperature-dependence of ψ_∞.

Variation of rate-constant with temperature.

In fig. 4 the rate-constant for the fastest rate observed at each experimental temperature is plotted in the form log k^* against T_∞^{-1}. Between

TABLE III. The fastest rate-constants, k^*, together with the fastest (k^*) and average ($\bar{k}$) constants corrected to $p_{H_2O} = 14\,000$ lb./in.^{2}

T (°C.)	$10^4 . T^{-1}$ (K^{-1})	p_{H_2O} (lb./in.^{2})	log k^*	log $\bar{k}^*$ at 14 000 lb./in.^{2}	log $\bar{k}$ at 14 000 lb./in.^{2}
1 000	7·86	2 000	0·66	1·08	$0·75 \pm 0·51$
900	8·53	7 000	0·78	0·93	$0·46 \pm 0·32$
850	8·90	14 000	0·79	0·79	$0·01 \pm 0·60$
800	9·32	14 000	0·03	0·03	$\bar{1}·43 \pm 0·49$
750	9·78	14 000	$\bar{1}·32$	$\bar{1}·32$	$\bar{1}·09 \pm 0·18$
700	10·28	28 000	$\bar{2}·88$	$\bar{2}·73$	$\bar{2}·52 \pm 0·17$
600	11·46	14 000	$\bar{2}·67$	$\bar{2}·67$	$\bar{2}·38 \pm 0·18$
550	12·15	14 000	$\bar{2}·73$	$\bar{2}·73$	$\bar{2}·27 \pm 0·27$
525	12·53	14 000	$\bar{2}·45$	$\bar{2}·45$	$\bar{2}·03 \pm 0·45$
525	12·53	7 000	$\bar{2}·28$	$\bar{2}·43$	$\bar{2}·24 \pm 0·20$
500	12·94	14 000	$\bar{3}·81$	$\bar{3}·81$	$\bar{3}·51 \pm 0·18$
475	13·37	14 000	$\bar{3}·08$	$\bar{3}·08$	$\bar{3}·02 \pm 0·05$
450	13·83	14 000	$\bar{4}·89$	$\bar{4}·89$	$\bar{4}·63 \pm 0·28$

900° C. and 700° C. log k^* decreases linearly with increasing T_∞^{-1}. A good linear relationship likewise holds between 550° C. and 450° C. The two lines differ little in slope, but the low-temperature line has a much larger intercept on the log k^*-axis. No error can be put on the values of log k^* because they represent *limiting* rates. The existence of straight-line relationships is in itself justification for paying special attention to such limiting fastest rates.

A marked break occurs in the plot in the region between 700° C. and 550° C., and must indicate the presence of a thermal transformation of some considerable magnitude in this temperature range. Rate of change of obliquity is greatly increased on passing down through the transformation; points lying on the low-temperature line correspond to rates about 500 times faster than would be indicated by the extension of the high-temperature line below the transformation temperature. Evidence that the transformation is smeared is provided by the situation of the experimental point for 600° C. between the two lines. The temperature limits of the smeared transformation cannot be evaluated from the available data, but may be regarded as lying in the range 575° C. to 625° C.

The mean rate constant $\bar{k}$, also shown on fig. 4, plots systematically below k^*, shows a marked break between 700° C. and 550° C., and is appaerntly subject to rather more pronounced smear.

The experimental point for 1 000° C. is aberrant. Inaccuracy inherent in the smallness of $(\psi_0 - \psi)$ and $(\psi - \psi_\infty)$ over the whole time-range at 1 000° C., proximity to the melting-point (1 118° C.), and possible

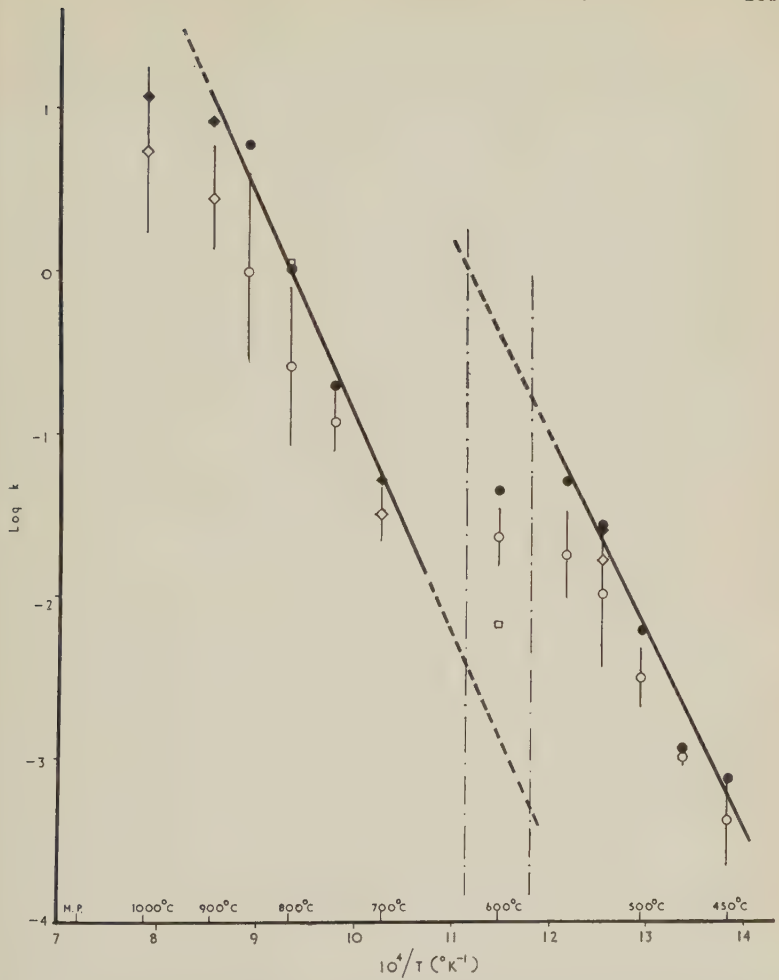

FIG. 4. Plot of log k against T^{-1}. ● refers to maximum rate constants (k^*), and ◊ to average rate constants ($\bar{k}$) at p_{H_2O} 14 000 lb./in.² in the main series. ◆ refers to maximum rate constants, and ◊ to average rate constants corrected to p_{H_2O} 14 000 lb./in.² from other pressures. □ refers to the reheating experiments 1 and 2 of table V.

involvement in the analbite → monalbite inversion may explain its departure from the high-temperature line.

Activation energies. The linear sections of the plot of log k^* against T^{-1} can be interpreted in terms of the Arrhenius equation

$$\ln k = B - E/RT \qquad (6)$$

in which R is the gas constant, and B and E are independent of temperature to a first approximation. The validity of the application of the Arrhenius equation to the rate of a solid-state reaction followed by measurements of a physical variable lies in the excellence of the fit of the data to the equation in the temperature ranges 900° C. to 700° C. and 550° C. to 450° C. Analogous use of the Arrhenius equation in the study of a solid state transformation has been made by McKie (1959) in the study of the low → high inversion in yoderite.

The activation energy E, which is a measure of the height of the energy barrier involved in the process responsible for the variation of obliquity, can be obtained from the slope of the linear portions of the graph of fig. 4, and is given by (slope) $\times R$ log e. Above the transformation, between 900° C. and 700° C., $E = 61{\cdot}6 \pm 0{\cdot}2$ kcal. mole^{-1}. Below the transformation, between 550° C. and 450° C., $E = 55{\cdot}9 \pm 0{\cdot}2$ kcal. mole^{-1}. The values[1] of E have been calculated from a regression of log k on T^{-1}, and the limits quoted are standard deviations.

Variation of rate with pressure.

The effect of varying p_{H_2O} may be to alter the limiting obliquity ψ_∞ and to alter the rate constant itself. Although the data are rather scanty some attempt has been made to evaluate both of these effects.

Values of ψ_∞ for runs at two pressures at 525° C. are listed in table II. The value of ψ_∞ for p_{H_2O} 28 000 lb./in.^{2} at 700° C. is also given in table II, and may be compared with the value ψ_∞ 1·825 for 14 000 lb./in.^{2} read from the smooth curve of fig. 3 at the same temperature. These are the only two items of experimental data relating ψ_∞ to p_{H_2O}. A simple, reasonable assumption would seem to be that the fractional change in ψ_∞ is proportional to the fractional change in p_{H_2O}, the coefficient of proportionality being determined by the two experimental points. The value of ψ_∞ at a pressure p is then given by

$$\psi_\infty(p) = \psi_\infty(p_s)\{1 - 0{\cdot}024(p - p_s)/p_s\}, \qquad (7)$$

where p_s is 14 000 lb./in.^{2} This relationship leads to values of ψ_∞ at 900° C. and 1 000° C. for p_{H_2O} 14 000 lb./in.^{2} that would lie fairly well on the smooth curve of fig. 3.

The variation of rate constant with p_{H_2O} can be considered in terms of an expression of the form $k = k_p \cdot p^n_{H_2O}$, where k_p is a rate constant inde-

[1] Though conventionally referred to as kcal. per mole, the units would be more exactly described as kcal. per formula-weight; there can be no true mole of a tectosilicate.

pendent of p_{H_2O}; k_p is also independent of total pressure since in all MacKenzie's experiments total pressure is equal to p_{H_2O}. Significant values of n will be zero, or some simple fraction, or some small integer. The expression is most conveniently considered in the form

$$\log k = \log k_p + n \log p_{H_2O}. \tag{8}$$

Values of $\log k$ are plotted against $\log p_{H_2O}$ for all the relevant data in fig. 5.

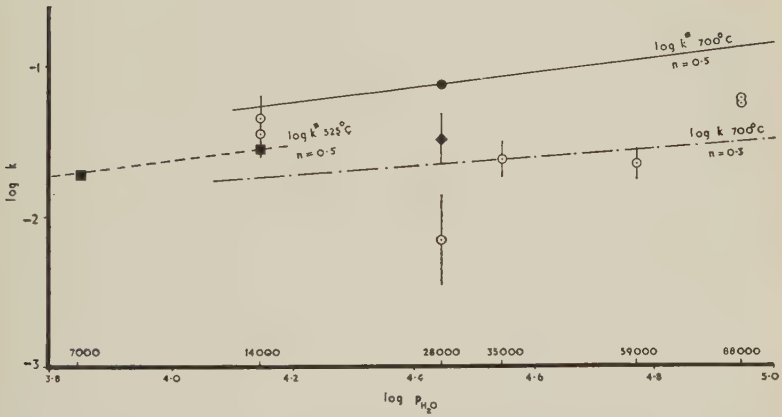

FIG. 5. Variation of rate constant with p_{H_2O}. ⊙ experimental points at 700° C. for $t = 16$ hours, with observational error. ♦ $\log \bar{k}$ at 700° C. with standard deviation. ● $\log k^*$ for fastest rate at 700° C. ■ $\log k^*$ for fastest rates at 525° C. —— limiting line of fastest rate at 700° C. drawn with $n = \frac{1}{2}$. – – line of fastest rate at 525° C. —·—· line of best fit for $t = 16$ hours at 700° C.

MacKenzie (1957, p. 488) performed a special series of experiments at 700° C. to investigate the effect of p_{H_2O}. Values of ψ_∞ calculated by use of equation (7), and of $\log k$ calculated by use of equation (3) are listed for each of these experimental points in table IV, and $\log k$ is plotted in fig. 5. The values of $\log k$ are given with observational error. A difficulty in interpreting these results is that very short times were used and consequently the observational error is large. Whatever hypothesis is used to describe the variation the points at 7 000 lb./in.^{2} appear to be aberrant; they are in any case subject to particularly large observational error. The points at 28 000 lb./in.^{2} yield values of $\log k$ lying outside the standard deviation of $\log \bar{k}$ for the same temperature and pressure (table III). The regression line of $\log k$ on $\log p_{H_2O}$ fitted to the experimental points between 14 000 and 88 000 lb./in.^{2} has n=0·3 with

TABLE IV. Variation of k with p_{H_2O}.

700° C., t = 16 hours, $\psi_0 = 1{\cdot}966$

p_{H_2O} (lb./in.²)	ψ_∞	log k (for each experiment)
7 000	1·847	$\bar{2}{\cdot}92 \pm 0{\cdot}20$, $\bar{2}{\cdot}62 \pm 0{\cdot}42$
14 000	1·825	$\bar{2}{\cdot}55 \pm 0{\cdot}16$, $\bar{2}{\cdot}65 \pm 0{\cdot}15$
28 000	1·782	$\bar{3}{\cdot}84 \pm 0{\cdot}30$ (twice)
35 000	1·759	$\bar{2}{\cdot}38 \pm 0{\cdot}12$ (twice)
59 000	1·684	$\bar{2}{\cdot}35 \pm 0{\cdot}10$ (twice)
88 000	1·593	$\bar{2}{\cdot}79 \pm 0{\cdot}02$, $\bar{2}{\cdot}76 \pm 0{\cdot}02$

700° C.—fastest rate

p_{H_2O} 28 000 lb./in.² log k^* $\bar{2}{\cdot}88$

525° C.—fastest rate

p_{H_2O} 7 000 lb./in.² log k^* $\bar{2}{\cdot}28$

p_{H_2O} 14 000 lb./in.² log k^* $\bar{2}{\cdot}45$

a standard deviation $\pm 0{\cdot}3$, and does not distinguish between the simple cases of $n = 0$ and $n = \frac{1}{2}$. In spite of their scatter the points do, however, all lie beneath the line with $n = \frac{1}{2}$ through log k^* for the fastest rate at 28 000 lb./in.²

More reliable data on the variation of rate constant with p_{H_2O} is provided by the fastest rates for the two series of experiments (given in table III) at 525° C. The comparison of fastest rates is likely to be more accurate than the comparison of log k for individual experiments; ψ_∞ has, moreover, been obtained by considering each series in terms of equations (4) and (5). The relationship they exhibit (fig. 5) is consistent only with a value of $n = \frac{1}{2}$.

All the evidence is consistent with, and that for 525° C. points directly to, a relationship between rate constant and p_{H_2O} of the form

$$k = k_p \cdot \sqrt{p_{H_2O}}.$$

KINETIC ANALYSIS OF MACKENZIE'S OTHER EXPERIMENTS.

After concluding the description of his main series of experiments, MacKenzie (1957, pp. 500–505) described some other experiments, the kinetics of which may be considered in the light of our treatment of the main series. Only one experiment was performed for each set of physical conditions, and therefore we cannot evaluate log k^*, but must be satisfied with the lower accuracy of a comparison of log k calculated by means of equation (3) for each experimental point. In these experiments the limiting obliquity ψ_0 ceases to be a fictional obliquity extrapolated to zero time, but is the actual obliquity of the crystalline starting material at the beginning of the experiment. MacKenzie's data and the values of log k calculated therefrom are summarized in table V.

Subsequent hydrothermal treatment of synthetic transitional triclinic $NaAlSi_3O_8$. Synthetic material from runs at 600° C. and 800° C. was reheated at 800° C. and 600° C., respectively, the same p_{H_2O}, 14 000

TABLE V. Data on heat treatment of synthetic and natural $NaAlSi_3O_8$.

	Initial crystallization			Subsequent heat treatment				
	T (°C.)	p_{H_2O} (lb./in.²)	ψ_0	T (°C.)	p_{H_2O} (lb./in.²)	t (hours)	ψ	$\log \lvert k \rvert$
1.	600	14 000	1·844	800	14 000	92	1·897	0·07
2.	800	14 000	1·930	600	14 000	162	1·885	$\bar{3}$·84
3.	850	14 000	1·951	1 080	dry	168	1·988	$\bar{2}$·81
4.	850	14 000	1·951	1 080	dry	504	2·008	$\bar{2}$·81
5.	800	14 000	1·921	1 080	dry	168	1·964	$\bar{2}$·54
6.	800	14 000	1·921	1 080	dry	504	1·985	$\bar{2}$·41
7.	750	14 000	1·890	1 080	dry	168	1·963	$\bar{2}$·66
8.	750	14 000	1·890	1 080	dry	504	1·962	$\bar{2}$·18
9.	600	14 000	1·805	1 080	dry	168	1·911	$\bar{2}$·37
10.	600	14 000	1·805	1 080	dry	504	1·925	$\bar{2}$·01
11.	Natural Amelia albite		1·060	800	14 000	90	1·848	$\bar{1}$·27
12.			1·060	800	14 000	311	1·844	$\bar{2}$·69

Experiments 1 and 2 are described on p. 504, 3–10 on p. 501, and 11 and 12 on p. 502 of MacKenzie (1957). The rate-constant is written $\log \lvert k \rvert$ because both k and $\psi_0 - \psi_\infty$ are negative, except in experiment 1, since obliquity is increasing with time instead of decreasing as in the main series of experiments.

lb./in.², being applied during preparation and subsequent heat treatment. The rate-constants for the subsequent heating are plotted in fig. 4, and it can be seen that they are not markedly divergent from the rate-constants for the main series of experiments at the same temperature and p_{H_2O}. They do not yield any kinetic evidence of the non-isothermal history of the material, and merely correspond to equilibration under the conditions of reheating. It is significant that the rate-constant for increasing obliquity at 800° C. should correspond so closely to that for decreasing obliquity in the main series experiment at the same temperature.

Dry heating of synthetic transitional triclinic $NaAlSi_3O_8$. Synthetic material prepared isothermally at various temperatures in the range 600° C. to 800° C. was heated dry at 1 080° C. at atmospheric pressure. The obliquity increased in each case towards the value expected for ψ_∞ at 1 080° C., which will approach ψ 2·03 of high albite. Rate constants have been calculated for each experimental point, assuming a value of 2·030 for ψ_∞, and are plotted against temperature of preparation in fig. 6. It is observed that in general, the higher the temperature of preparation of the synthetic material, the higher is the rate constant for equilibration under dry conditions at high temperature. The amount of the departure of the synthetic $NaAlSi_3O_8$ from the equilibrium obliquity appropriate to its temperature of preparation appears to have no systematic effect on the rate constant for dry reheating.

The observed rates ($\bar{2}{\cdot}0 \leqslant \log k \leqslant \bar{2}{\cdot}8$) are 200 to 2 000 times slower

than the rate of equilibration ($\log k \simeq 1{\cdot}2$) inferred from fig. 4 and equation (8) for 1 080° C., p_{H_2O} 14·7 lb./in.^{2} Two factors may be responsible for the slowness observed: firstly, the absence of water; and secondly, the starting material was a glass, which crystallized and equilibrated at the

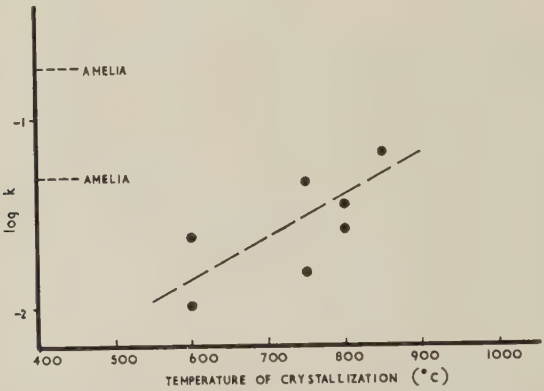

FIG. 6. Graph of rate constant against temperature of crystallization for dry heating at 1 080° C. of synthetic transitional triclinic $NaAlSi_3O_8$. Broken lines represent rate constants for dry heating of Amelia albite.

same temperature and p_{H_2O}. The results discussed in the previous section make it clear, however, that it is absence of water that is primarily responsible for the slowness of dry equilibration.

Hydrothermal treatment of Amelia albite. MacKenzie's two experiments show an increase in obliquity towards the value of ψ_∞ 1·905 corresponding to the experimental conditions, 800° C., p_{H_2O} 14 000 lb./in.^{2} The rate constants are smaller: 0·2 and 0·05 times k^* for the fastest equilibration of synthetic triclinic $NaAlSi_3O_8$ under like conditions. The slowness of hydrothermal equilibration may be due in part to neither experiment happening to display the fastest rate, and in part to the presumably very low equilibration temperature of the natural pegmatitic material.

Discussion.

Comparison of 'wet' and 'dry' equilibration rates. MacKenzie has noted (1957, p. 505) that synthetic transitional $NaAlSi_3O_8$ heated in the dry at 700° C. and 14 000 lb./in.^{2} did not show any measurable change in obliquity after 140 hours' treatment. He has also indicated that no

changes can be produced, in laboratory time, in either low-temperature albites or synthetic albites, except near the melting-point, unless water vapour is present.

It is convenient to discuss separately the possible effects of hydrostatic pressure and water vapour pressure. In general the hydrostatic pressure dependence of solid diffusion processes is likely to be small. Some change in rate in a solid state reaction may be produced if the stability of the equilibrium phase or phase assemblage is favoured by increased hydrostatic pressure, but in the absence of this effect increase in pressure may in practice decrease the rate of diffusion in much the same way as increase in pressure increases the viscosity of liquids (Glasstone, Laidler, and Eyring, 1941, p. 541). These considerations suggest that the hydrostatic pressure dependence of equilibration rates in the case of triclinic $NaAlSi_3O_8$ is likely to be small.

The observed change in equilibration rates under dry and hydrothermal conditions must necessarily be associated with the direct participation of water or its dissociation products in the mechanism of the transformation process. Such participation necessarily defines a change in the free energy of activation for the transformation process.

The dependence of equilibration rates on water vapour pressure. Analysis of the p_{H_2O}-dependence of the rate of transformation has been given in a previous section. The analysis, particularly in the case of experiments at 525° C., indicates that the rates depend on the square root of the total water-vapour pressure. Such relationship would be consistent with the direct participation of H^+ in the transformation process since the activity of H^+ in the vapour phase bears a corresponding relationship to the total water-vapour pressure.

The hydrogen-ion concentration in the vapour phase can only be relevant in the transformation mechanism if the solid is capable of ion exchange with the vapour phase. The necessary ion-exchange process may be considered a type of hydrolytic equilibrium: the exchange process being comparable with the hydrolysis of $AlSi_3O_8^-$ in the vapour.

Equilibrium between the vapour and the solid may be written:

Na^+	OH^-	H^+	
			$AlSi_3O_8^-$
H_3O^+		Na^+	
VAPOUR		SOLID	

If the equilibrium constant for the ion-exchange process and the

dissociation constant for water are not materially affected by the change in pressure involved, the proton concentration in the solid will be proportional to the square root of the total water vapour pressure.

The activation energy for the process of transformation in triclinic $NaAlSi_3O_8$, as already noted, is of the order of 60 kcal./mole. In the absence of more data on the precise mechanism of the transformation process it would be incorrect to identify this energy with any specific mechanism, but it may be equated, in a general way, with a rate-controlling diffusion mechanism involving Al–Si ordering in the structure. The data of Pauling (1940, p. 53) indicate that the Si–O bond energy is of the order of 90 kcal./mole. The activation energy for the removal of Si from an SiO_4 tetrahedron must be of approximately equal magnitude. Data on the diffusion of sodium in compounds of similar type indicate a much lower activation energy, of the order of 20 kcal./mole.

The rapidity of the ordering process in triclinic $NaAlSi_3O_8$ under hydrothermal conditions must be related to the provision of a suitable mechanism for the ordering process.

Structural aspects of the transformation. Ferguson, Traill, and Taylor (1958) have given detailed accounts of the structures of both high- and low-albite. In high-albite the structural data indicate that Al and Si have an apparently random distribution over available tetrahedral sites and that the sodium atom in the averaged cell appears to occupy an ellipsoidal volume which may represent a time or space average over different positions. The authors suggested the possibility of two distinct sites for the sodium atom. From a study of the tetrahedral bond-lengths in low-albite Ferguson and others suggested that the major part of the Al was present on one of the four symmetrically distinct tetrahedral sites and that the 'average' volume occupied by the sodium atom was much smaller.

The structural data and the present kinetic analysis present independent and compatible evidence on the role of Al–Si ordering in the high–low albite transformation. The role of Al Si ordering should not, however, be emphasized to the exclusion of other possible aspects of the transformation. Clearly the role of the sodium atom is also of considerable importance.

The kinetic analysis provides important evidence on the degree of continuity of the ordering process in triclinic $NaAlSi_3O_8$ as a function of temperature. Slow change in the obliquity in the temperature ranges above 650° C. may define a change in the degree of Al Si order in this temperature range. In the region of 600° C. a rapid change in the degree

of order of Al and Si is implied. This change possibly comes close to being discontinuous and may, at present, be conveniently described as a smeared transformation. Below 500° C. there appears to be further change in obliquity defining further change in the degree of Al–Si order.

Petrological considerations. The immediate petrological applications of this study are limited, but clearly the occurrence of low-albite in rocks implies either crystallization below the transformation temperature or the inversion of high-albite by slow cooling under hydrothermal conditions through the critical temperature range about 600° C. where the rates of transformation are fast. The structural state of low-albite may be expected to be influenced in detail by differing physical conditions of crystallization and cooling rate; such differences in adjustment towards the low-temperature equilibrium state are implicit in the different dry-heating behaviour of low-albite from various localities, even though detailed structural analyses of materials of varying origin are lacking. The rarity of high-albite in nature ($Ab \geqslant 95$) is to be ascribed perhaps in part to the high rate of transformation to the low-temperature modification around 600° C.

It would be of some interest to follow the transformation at 600° C. away from the albite composition and to examine its participation in peristeritic exsolution, its bearing on the general problem of the intermediate plagioclases, its influence on the alkali–feldspar solvus and in the wider field of the silica–nepheline–kalsilite system.

General conclusions. The existence of a smeared transformation in triclinic $NaAlSi_3O_8$ has been recognized by examination of the temperature variation of rate of transformation, and it would therefore seem appropriate to stress the usefulness of a kinetic approach to certain feldspar problems and to polymorphic transformations in general. The study of the rate of approach to equilibrium provides information on the mechanism of the process that cannot be derived from the mere observation of equilibrium. Moreover, if the mechanism of reaction or inversion is known, extrapolation to experimentally unattainable conditions may be attempted and some explanation offered for natural cases of non-equilibrium. In general the interrelations of feldspar phases in a rock should be considered on a time–temperature basis, rather than on the assumption of complete equilibration down to some minimum temperature below which no change occurred. But in interpreting natural processes in terms of experimental hydrothermal data it must also be borne in mind that variation of catalyst may exert a profound influence on the mechanism by which a reaction or polymorphic inversion takes

place. Such considerations may even determine the accessibility of the true equilibrium state.

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What is plinthite?

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[Taken as read 31 March 1960.]

Summary. Many specimens of plinthite, a species described from Co. Antrim by T. Thomson in 1836 and later from Skye by M. F. Heddle, prove to be mixtures of zeolites and hematite. Both original analyses are those of a ferruginous clay (a mixture of hematite, kaolinite, and montmorillonite). The type specimen (Thomson Collection) is a red clay in the montmorillonite group intimately mixed with hematite and a little analcime.

In 1836 Thomas Thomson described a new mineral from Co. Antrim that he called plinthite (from πλίνθος) on account of its brick-red colour.[1] Its texture was earthy; fracture flat, conchoidal; hardness 2·75; and sp. gr. 2·342.

In 1880 M. F. Heddle described a similar substance, deep red in colour with a greasy lustre or earthy and dull, from The Quirang in Skye.[2] A more detailed description of this occurrence is given in a paper published in 1883.[3] At this locality he found plinthite occurring in three forms: in beds of a few inches to nearly a foot in thickness, which he thought might have been formed by the alteration of loam by a lava stream; in rough radiating spheres about the size of a pea; and in thin layers or bands occurring with zeolites (chabazite, 'red mesolite',[4] thomsonite, analcime), calcite, saponite, and apophyllite. This last occurrence he thought so unusual that he analysed the material and found it compared favourably with T. Thomson's plinthite.

In Skye, particularly near Uig, there are lumps of a massive red mineral that look like hematite. This proved to be a mixture of hematite and chlorite (B.M. 1959, 571) but it turned my attention to plinthite and I determined to try to solve its identity. As Thomson was Professor of Chemistry in Glasgow University and his nephew was his chief analyst, it seemed possible that some of his material might be

[1] T. Thomson, Outlines of Mineralogy, Geology, and Mineral Analysis, 1836, p. 323.

[2] M. F. Heddle, Min. Mag., 1882, vol. 5, p. 26.

[3] M. F. Heddle, Min. Mag., 1883, vol. 5, p. 117.

[4] See p. 457, below.

in the Hunterian Museum, but his collections do not appear to have been preserved there.

After much searching, a specimen of plinthite (1960.10.1) from the Thomson Collection was found in the Royal Scottish Museum. It bears the label 'Plinthite Co. Antrim' on which is superimposed a red ticket with the initial T. On comparison with other specimens in the collection this was found to mean 'Thomson', although it had not been previously recognized as such. The Royal Scottish Museum has only a few specimens belonging to the Thomson Collection and how these came there is not yet known. The type specimen consists of masses of a shiny deep-red mineral (A) in close association with an earthy pale-red mineral (B), veined with fibrous, nodular, and massive natrolite together with some of the parent basalt; the mineral A is a clay belonging to the montmorillonite group ($1{\cdot}524 > n > 1{\cdot}517$) intimately mixed with hematite and a little analcime (X-ray no. 8806); the mineral B (X-ray no. 8807; $1{\cdot}517 > n > 1{\cdot}497$) is granular analcime. Another specimen from the Royal Scottish Museum Collection (1847.17.1; Patrick Doran no. 19) from Co. Antrim consists of red and white nodules in basalt associated with well-developed acicular natrolite; the red material of the nodules (X-ray no. 8805) is analcime with a little clay and the white is natrolite. In the British Museum Mineral Collection a pale-red rough massive specimen of plinthite from Co. Antrim (B.M. 89894)[1] proved to be a fine-grained mixture of thomsonite and chabazite. A specimen from Co. Antrim[2] in the Natural History Department of the Glasgow Art Gallery and Museum also proved to be a mixture of thomsonite and chabazite (X-ray no. 8738).

Heddle's material from Skye is preserved in the Royal Scottish Museum and has been made available for examination. There are two specimens (S.M.C. 493 A1 and 493 A2) from the Echoing Rock near Fir Breugach, about a mile north of The Quirang, which tally very closely with his description of the second variety: they are brick-red but the radiating appearance is only superficial; X-ray determination (X-ray nos. 8625, 8622) showed them to be a mixture of thomsonite and hematite. S.M.C. 493 A3 from The Storr, a dull-red massive specimen, not entirely homogeneous, is a mixture of analcime and hematite (X-ray no. 8624) with inclusions of thomsonite. The fourth specimen (S.M.C. 493 A4) is labelled in Heddle's handwriting 'Bole between Uig and

[1] Allan-Greg Colln.: obtained by R. P. Greg between 1848 and 1851.

[2] No. 02–161 abw. Presented by Major A. J. Fleming, 1901 (probably collection of Professor John Fleming (1785–1857) of Aberdeen).

Stainshal [= Stenscholl], Skye'; this is dark-red, smoother in texture than the last and with a slightly conchoidal fracture; it is a mixture of thomsonite and hematite (X-ray no. 8626).

Here mention may also be made of Heddle's 'red mesolite'[1] from The Storr and The Quirang. Three specimens from the Royal Scottish Museum Collection have been examined. A massive red and cream mineral in basalt (S.M.C. 455.2) from the Echoing Rock, The Quirang, is a mixture of thomsonite and analcime, and another specimen from The Quirang (S.M.C. 455.13) occurring as nodules in basalt with thomsonite, analcime, stilbite, and apophyllite, is principally analcime. A third red and white massive mineral from The Storr, with analcime, thomsonite, and chabazite (S.M.C. 455.14), is a mixture of analcime and thomsonite. Heddle's analysis of 'red mesolite' (loc. cit.), which he says is sometimes confused with plinthite, agrees well with such a mixture.

There are three specimens in the Royal Scottish Museum (Patrick Dudgeon Collection) labelled 'plinthite' from The Quirang. These are light-red massive thomsonite with a little chabazite and analcime (1878.49.387); red massive (mixture of analcime and hematite) with thomsonite and analcime (1878.49.386); and red massive (mixture of analcime and thomsonite) with large white crystals of analcime and platy thomsonite (sphaerostilbite) in basalt (1878.49.388). Another 'plinthite' from an unknown donor (S.M.C. 493 A5) from The Storr is a flesh-coloured smooth clay on an altered ferruginous rock and proves to be kaolinite (X-ray no. 8623).

Two specimens of 'plinthite' from the James Currie Collection in Edinburgh University have also been examined. Currie helped with the posthumous production of Heddle's 'Mineralogy' and indeed went over much of the ground covered by Heddle, so his specimens are of considerable interest. They are both from The Quirang. One is a light-red aggregate and consists of thomsonite and hematite (X-ray no. 8737). The other is darker red with inclusions of analcime, chabazite, and earthy thomsonite on a zeolitic lava containing chabazite crystals; the red material is a mixture of thomsonite and hematite (X-ray no. 8736). A pale-pink rough specimen labelled plinthite in the Mineral Collection of the British Museum (B.M. 89893)[2] from The Quirang proved to be a mixture of thomsonite and analcime.

From this it seems obvious that the remains of Heddle's analysed material was lost and the only Heddle specimens that really correspond

[1] M. F. Heddle, Min. Mag., 1883, vol. 5, p. 118.

[2] Allan-Greg Colln.; obtained by R. P. Greg between 1848 and 1851.

to his description are the spherulitic masses from the Echoing Rock—which he did not analyse.[1] In this connexion it is interesting to note that Mr. W. F. Davidson, who has recently been collecting zeolites from The Quirang, had a specimen showing crystals of stilbite and chabazite occurring in basalt and lying on a blanket of a red waxy mineral, which also forms nodules in the rock (B.M. 1959, 280). This red mineral proved to be a member of the montmorillonite group and agrees quite well in description with Heddle's analysed plinthite.

The analyses of the plinthite are:

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	H_2O	Total
1.	30·88	20·76	26·16	—	—	2·60	19·60	100·00
2.	29·547	19·027	28·013	3·251	0·844	2·234	17·391	100·307

1. Co. Antrim. Analyst, T. Thomson, 1836.
2. The Quirang, Skye. Analyst, M. F. Heddle, 1880.

From both these analyses it can be deduced that the material analysed was, as Heddle suggested, a ferruginous clay, with a composition about hematite 26 %, kaolinite 40 %, and montmorillonite 34 %. In 1882 Heddle noted an occurrence of plinthite overlying lignite from under the 'Organ' at the Giant's Causeway in Co. Antrim[2] but gave no analysis. A specimen called 'levigated clay' from Giant's Causeway, Co. Antrim (B.M. 1944, 85), from the collection of Dr. John Lee (1783 1866) of Hartwell House, Aylesbury, is a mixture of hematite, kaolinite, and montmorillonite and could be taken as typical of material that was collected about the same period as Thomson's plinthite, with approximately the same composition.

From this it seems clear that Thomson applied the name to a ferruginous clay, but that massive red mixtures of zeolites were subsequently also styled 'plinthite'.

Acknowledgements. I should like to thank many curators who have searched their collections for 'plinthite', and especially Dr. C. D. Waterston of the Royal Scottish Museum, Professor F. H. Stewart of Edinburgh University, and Mr. G. R. Tresise of the Glasgow Art Gallery and Museum for permission to study their specimens from Skye and Co. Antrim, and also the members of our own X-ray department for their patience in interpreting many photographs.

[1] Heddle also noticed at The Quirang and even more abundantly at The Storr (Min. Mag., 1883, vol. 5, p. 119) a variety of thomsonite that has been called 'rock-soap'. It is, however, rough and not soapy in texture, and in appearance rather like kaolinite. The present writer found similar material near Uig, which when fresh was sugary and granular in appearance but on drying became more hard and compact. It was found to consist of a mixture of fine-grained analcime and thomsonite (B.M. 1959, 567) or just analcime (B.M. 1959, 568).

[2] M. F. Heddle, Min. Mag., 1882, vol. 5, p. 24.

The system CaO–MgO–FeO–SiO_2 and its bearing on the origin of ultrabasic and basic rocks.

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[Read 28 January 1960.]

Summary. Experimental data in the system CaO–MgO–FeO–SiO_2 suggest that there may be a plateau on the liquidus and solidus of the multicomponent system basalt–peridotite. If this is so, fusion of peridotite would produce only basaltic magmas over a wide temperature range; when the temperature reached a value such that the liquid crossed the threshold of the plateau, there would be a rapid increase in the amount of fusion for small temperature increases, with the formation of picritic magmas; basaltic magmas containing suspended forsteritic olivine crystals could dissolve them if the temperature rose slightly above that of the plateau threshold; a high proportion of a picritic magma would crystallize in a small temperature interval, with the precipitation of forsteritic olivine that was only slightly zoned. These possibilities are compared with current theories, and it is concluded that several petrological axioms may require critical re-examination. An experimental procedure is outlined to determine the shape of the liquidus and solidus in the basalt–peridotite system.

MANY ultrabasic rocks are composed almost entirely of the six oxides SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, and CaO. Phase relations in systems involving these oxides have been studied with special reference to steel plant refractories and slags (Osborn, 1954) and, although the compositions of interest to the steel industry do not always coincide with those of interest to petrologists, parts of the systems studied in most detail correspond closely to the compositions of some ultrabasic rocks. Of particular interest is Ricker's (1952) study of the system CaO–MgO–FeO–SiO_2.

The term 'ultrabasic' embraces many different rock types, which occur in a wide variety of field and petrographic associations. The present communication is concerned only with the origin of olivine-rich rocks, but even with this limitation there remain to be considered many different field associations. The following discussion is most relevant to rocks that occur in a volcanic association, e.g. the minor intrusions of picrite and peridotite in Skye (Harker, 1904; Bowen, 1928; Drever and Johnston, 1958), the sheets of picrite on Ubekendt Ejland, West Green-

land (Drever, 1956), and many olivine basalts of the world. Field and petrographic studies of picritic rocks have cast doubt on the adequacy of the hypothesis of olivine accumulation from basaltic magma to explain their origin (Drever, 1952, 1956; Drever and Johnston, 1958; Wyllie, 1958*a*). There is much evidence indicating that accumulation of olivine crystals does occur during the crystallization of basaltic magma, but this does not mean that olivine-rich and ultrabasic rocks may not be derived from other sources, and by other means. In view of the complexity of magmas and magmatic processes, it appears unjustifiable to erect a single hypothesis for the origin of all ultrabasic rocks in their many and varied occurrences.

Experimental studies demand a very high temperature for the existence of ultrabasic liquids, which is one reason why many petrologists classify all ultrabasic rocks as accumulates (Bowen, 1928). This prompted a search of the available phase-equilibrium data for alternative possibilities.

Phase equilibrium studies and the melting temperatures of olivine-rich rocks.

Reviews of ultrabasic rocks generally refer to their low intrusion temperatures. According to Turner and Verhoogen (1951, p. 243) the intrusion temperature of peridotites in the orogenic zones 'is commonly, if not always, of the order of a few hundred degrees'. There is a tendency to overlook the fact that other ultrabasic rocks show evidence of higher intrusion temperatures. For instance, some of the peridotites in Skye were hotter than gabbros when emplaced (Harker, 1904, 1909), and some of the minor intrusions of picrite on Soay were apparently emplaced at relatively high temperatures (Wyllie, 1958*a*, 1958*b*). There appears to be no field evidence to support the contention of Vogt (1922) that dunites and peridotites were emplaced as very hot liquid magmas with temperatures near 1 600° C.

Forsterite melts at 1 890° C., and available experimental data suggest that ultrabasic liquids, rich in forsterite, can exist only at very high temperatures. Vogt suggested that addition of fayalite to forsterite might cause marked lowering of liquidus temperatures, but subsequent study of the system MgO–FeO–SiO_2 (Bowen and Schairer, 1935) proved that a temperature of 1 800° C. was required for the complete melting of olivine up to $Fo_{80}Fa_{20}$ in composition. Osborn and Tait (1952) found that in the system diopside–anorthite–forsterite, although some liquid developed at rather low temperatures (1 270° C.) for mixtures rich in forsterite, the amount of liquid remained very small until high tempera-

tures were reached. Harker (1909) believed that many ultrabasic rocks were emplaced as liquid magmas, and that the addition of volatiles would aid the liquefaction of accumulated olivine crystals at moderate temperatures (oral communication to Bowen, 1928, p. 166), but he realized the difficulty of visualizing a process whereby volatiles could be added to a largely crystalline mass. In order to explain certain field relationships of peridotites in orogenic zones, Hess (1938) postulated that these rocks were emplaced, at low temperatures, as aqueous ultrabasic liquids derived by fusion of the ultrabasic substratum. Investigation of the system MgO–SiO_2–H_2O (Bowen and Tuttle, 1949) does not support this view. No liquid phase was developed below 1 000° C. at pressures up to 30 000 lb./sq. in., and the effect of water vapour on the melting relations of ultrabasic compositions remains uncertain. Bowen and Tuttle concluded that intrusion of a crystal mush was the most likely mechanism for the emplacement of ultrabasic rocks. Hess (1955) pointed out the difficulties inherent in this mechanism of intrusion, and he believes that the field evidence for magmatic origin should take precedence over experimental evidence.

Ricker (1952) discovered that the addition to forsterite of calcium orthosilicate (larnite) as well as fayalite does cause a marked lowering of liquidus temperatures. Since olivine-rich rocks (dunites excepted) contain appreciable amounts of CaO and FeO it seems that they could exist as liquids at temperatures lower than previously suspected from experimental data. Liquidus temperatures in relevant parts of the system CaO–MgO–FeO–SiO_2 are nevertheless much higher than estimated intrusion temperatures of ultrabasic rocks.

CaO–MgO–FeO–SiO_2 and related systems.

The phase relations in a quaternary system may be represented by a tetrahedron whose four corners represent the four components. Fig. 1 shows the system CaO–MgO–FeO–SiO_2; only selected compounds and joins are illustrated. For olivine-rich rocks, the orthosilicate join is of greatest interest. Phase relationships for this join were determined by Ricker (1952); primary crystallization fields and isotherms for the liquidus and solidus surfaces are reproduced in fig. 2*a*. Tie-lines for coexisting liquids and crystals were not determined, but the position of the solidus was located in parts of the system and sketched approximately elsewhere (dotted lines). Three primary phase fields appear on the join, and the field of olivine is by far the largest.

There is a temperature valley on both liquidus and solidus surfaces of

the olivine field, extending initially from $2MgO.SiO_2$ (forsterite) towards $CaO.FeO.SiO_2$. In the central part of the diagram, the valley opens out into a plateau of considerable extent, and from this plateau the valley

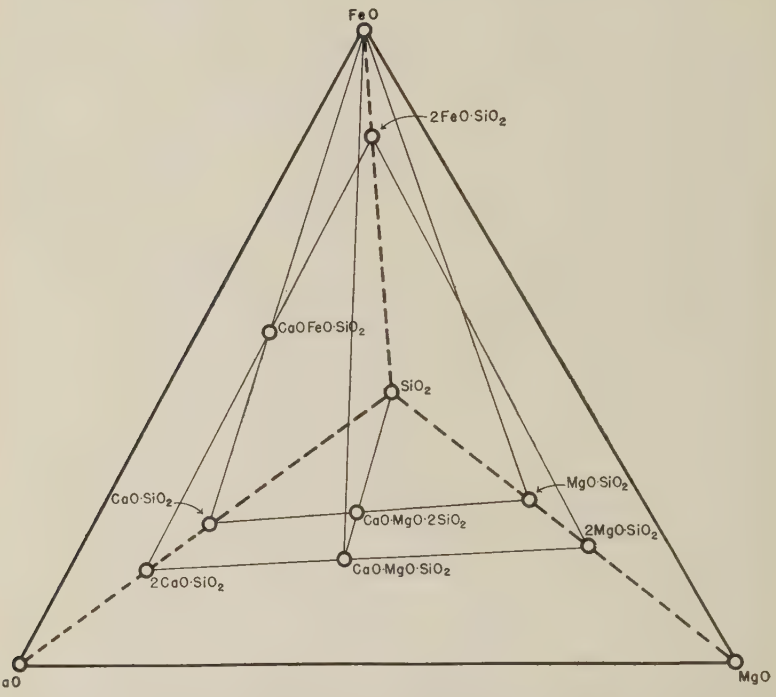

FIG. 1. Tetrahedron representing the quaternary system CaO–MgO–FeO–SiO_2. Compounds are plotted in weight % of the four components. Lighter lines bound triangular joins (after Ricker, 1952).

continues towards the temperature minimum on the join $CaO.FeO.SiO_2$–$2FeO.SiO_2$. The rapid lowering of liquidus temperatures produced by the addition of $CaO.FeO.SiO_2$ to $2MgO.SiO_2$ is well illustrated by the section across the olivine join shown in fig. 2*b*. In this section, compositions containing almost 60 weight % of forsterite are completely liquid at 1500° C. The effect of adding CaO and Al_2O_3 to forsterite is less marked; in the system diopside–anorthite–forsterite (Osborn and Tait, 1952), compositions containing 60 weight % of forsterite are completely liquid only above 1600° C., and in the binary system $2MgO.SiO_2$ a temperature of about 1730° C. would be required to liquify a composition containing 60 weight % forsterite (fig. 2*a*).

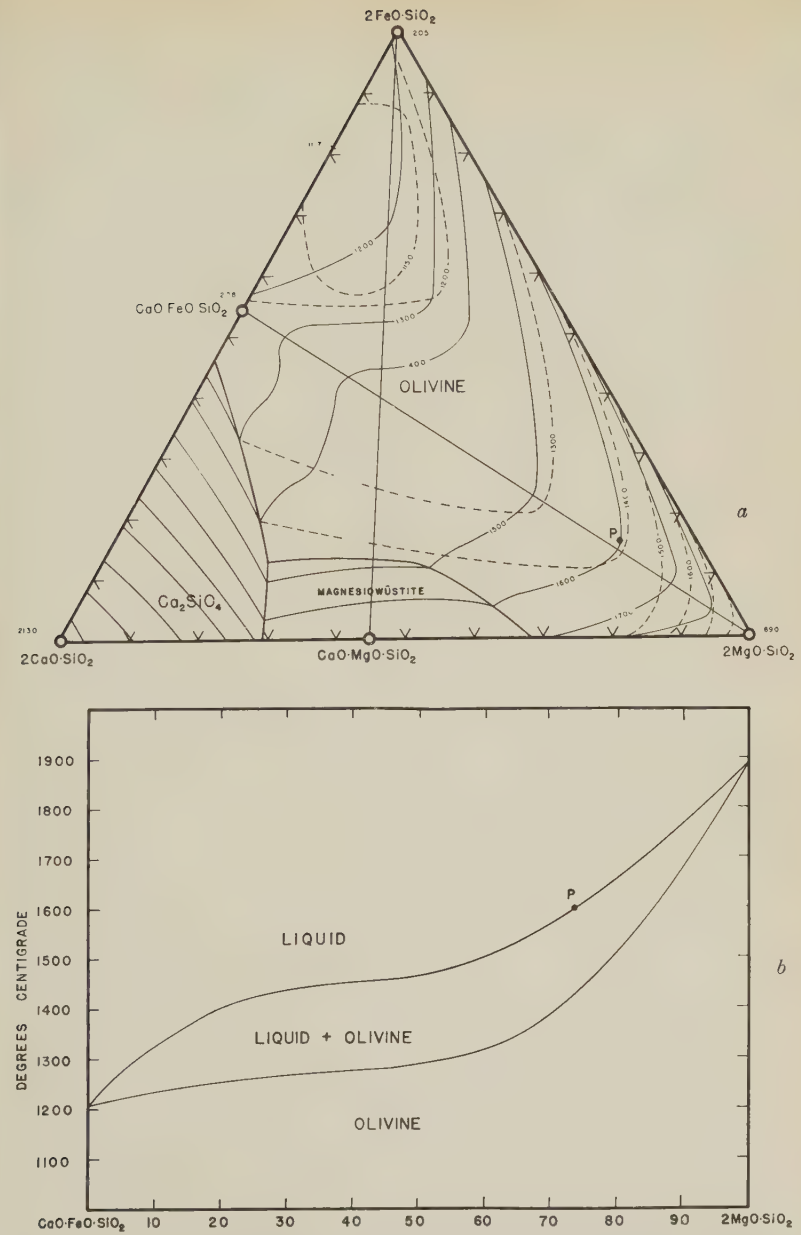

FIG. 2. *a*. Equilibrium diagram for the olivine join in the quaternary system $CaO–MgO–FeO–SiO_2$. Heavy lines are boundary curves; light lines are isotherms; light dashed lines are solidus isotherms in the olivine field. *b*. Liquidus and solidus intersections for the join $2MgO.SiO_2–CaO.FeO.SiO_2$. This section is not a binary system. P is the point representing the composition of an analysed picrite: all MgO, FeO, and CaO were calculated as normative orthosilicate and recalculated to 100 % (both diagrams after Ricker, 1952).

The existence of such a large plateau on both liquidus and solidus surfaces of the orthosilicate join results in some rather unusual crystallization and fusion phenomena. With cooling, the composition of a liquid on the liquidus plateau could change considerably while the composition of the crystallizing olivine would change only slightly and, with heating, the composition of the crystalline material on the solidus plateau could change considerably while that of the liquid developed by fusion would change only slightly. These conditions can be illustrated by a section across the centre of the plateau (fig. 2*b*). This join is not a binary system because tie-lines connecting coexisting liquids and olivines do not lie in the plane of the section, but there is evidence that the tie-lines intersect the plane in quite small angles. The situation is further complicated by the fact that the orthosilicate plane itself is not ternary. However, for the purpose of discussion the join may be treated as a binary system of the type with complete solid solution between the end-members. The changing composition of olivine in fig. 2*b* then involves a variation in lime content. Accurate determination of the quaternary tie-lines between liquid and olivine would probably reveal a low content of lime in all crystals; olivines precipitated from basaltic magmas rarely contain more than 1 weight % CaO. Persistence of the plateau over a large part of the olivine field confirms the general applicability of the relations described below.

Consider a mixture in fig. 2*b* with composition forsterite 58% (58Fo). This would be completely liquid above 1500° C., and at 1500° C. crystals of 79Fo would appear. With further cooling, more olivine would be precipitated and the liquid composition would change down the liquidus surface; provided equilibrium were maintained, the composition of the crystals would change down the solidus surface. At 1400° C., about 75 % of the liquid would have crystallized and that remaining would have the composition 19Fo; the crystals would be 71·5Fo. At 1310° C., the last trace of liquid (composition 9Fo) would crystallize, leaving only olivine crystals, 58Fo. Thus, a change in temperature from 1500° C. to 1400° C. would cause the liquid to change composition from 58Fo to 19Fo, while 75 % of it crystallized, and the olivine precipitated from it would change only from 79Fo to 71·5Fo; and a change in temperature from 1400° C. to 1310° C. would cause the remaining 25 % of liquid to change composition from 19Fo to 9Fo (the last trace of liquid), while the olivine crystallizing changed from 71·5Fo to 58Fo. Similarly, if a crystalline charge with composition 58Fo were heated, the first trace of liquid, with composition 9Fo, would appear at 1310° C. In the

temperature interval 1310° C. to 1400° C. about 25 % of the charge would melt, and the liquid developed would change composition from 9Fo to 19Fo, while the olivine would change from 58Fo to 71·5Fo. In the temperature interval 1400° C. to 1500° C. the remaining 75 % of the solid would melt, the liquid changing in composition from 19Fo to 58Fo, while the olivine changed from 71·5Fo to 79Fo (the last crystal to melt).

Rocks may be projected on to the orthosilicate join by allocating all the CaO, MgO, and FeO in an analysis to normative orthosilicates, and recalculating to 100 %. If all available analyses of basic and picritic rocks for the Skye group of minor intrusions are projected on to the orthosilicate join in this way (fig. 3), they extend across the plateau from *P* to the 1400° C. isotherm (fig. 2*a*), and they are not far removed from the section $2MgO.SiO_2$–$CaO.FeO.SiO_2$. The point *P* (figs. 2 and 3) represents a picrite sill (Sill 1, Drever and Johnston, 1958; Wyllie, 1958*a*) composed of 61 modal % olivine, 22 % plagioclase, 14 % clinopyroxene, and 3 % spinel and serpentine. The compositional trend of the plotted rocks is shown by the curved line extending from *P* (fig. 3). The average magma types of the Hebrides (Turner and Verhoogen, 1951, p. 193) and the hypothetical parent magma of the Rhum layered intrusion (Brown, 1956) are plotted for comparison. The numbers alongside the points give values for the ratio $(FeO + Fe_2O_3)/(FeO + Fe_2O_3 + MgO)$.

The picrite *P* contains a small excess of SiO_2 over that required to convert the CaO, MgO, and FeO to orthosilicate, and a point representing its position within the quaternary tetrahedron therefore lies between the orthosilicate join and the SiO_2 corner (fig. 1). Basaltic liquids contain a fairly large excess of SiO_2 over that required to convert all CaO, MgO, and FeO to orthosilicate, and points representing basalts within the tetrahedron are therefore quite far displaced from the orthosilicate join towards the SiO_2 corner. Within the quaternary tetrahedron, therefore, the trend line projected in fig. 3 runs obliquely from the orthosilicate join towards the SiO_2 corner of the tetrahedron.

The plateau feature persists on liquidus surfaces near the metasilicate join, e.g. on the join $CaO.SiO_2$–$MgO.SiO_2$–FeO (fig. 1), and here the variation of liquidus temperature over the whole join is less than that over the orthosilicate join (Ricker, 1952). Fairly level areas persist also on liquidus surfaces in the system CaO–MgO–SiO_2, and on the 5, 10, and 15 % Al_2O_3 planes of the system CaO–MgO–Al_2O_3–SiO_2 (Osborn *et al.*, 1954). The level surfaces extend from the forsterite field across the field of pyroxene, with liquidus temperatures between 1400° C. and 1300° C., and on the 15 % Al_2O_3 plane the level area extends across the primary

fields of pyroxene and anorthite. There are obvious parallels between this variation and that between ultrabasic and basic rocks.

When they are plotted in terms of normative orthosilicate, the Skye rocks, ranging in composition from picrite to basalt, lie close to the

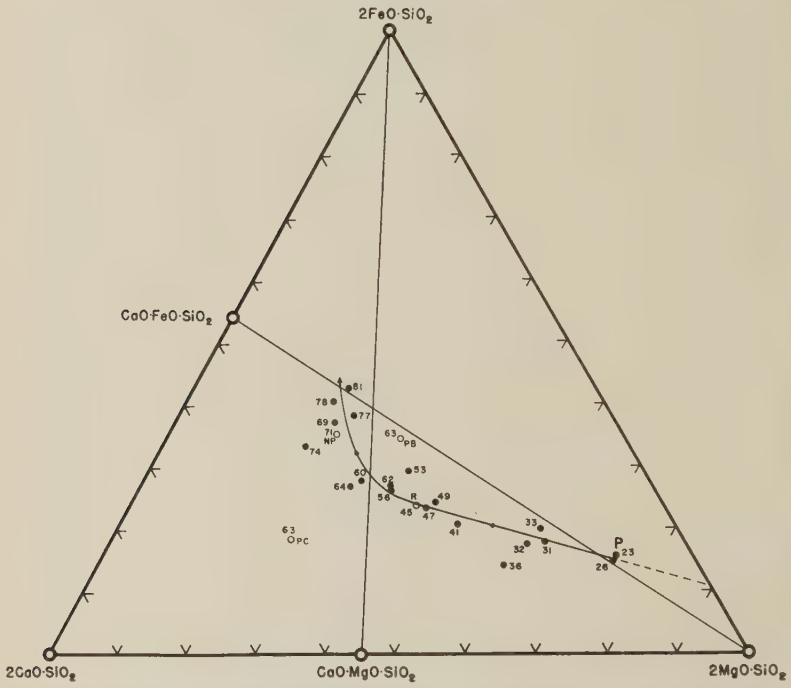

Fig. 3. Analyses of basic to ultrabasic rocks of the Skye region projected on to the orthosilicate join of the system CaO–MgO–FeO–SiO_2. The open circles represent the average plateau basalt (PB), non-porphyritic central magma type (NP), porphyritic central magma type (PC), and the hypothetical parent magma of the Rhum layered intrusion (R). The numbers give the values of the ratio $(FeO + Fe_2O_3)/(FeO + Fe_2O_3 + MgO)$ for each rock. The analyses are taken from Harker, 1904; Drever and Johnston, 1958; and Wyllie, 1958*a*. The line through the points is a projection of the chemical variation of the rocks from within the tetrahedron (fig. 1) on to the orthosilicate plane.

liquidus of the section illustrated in fig. 2*b*. Furthermore, the plateau feature appears to persist in those parts of the system CaO–MgO–FeO–Al_2O_3–SiO_2 that are chemically related to these rocks. If a similar plateau exists on the liquidus between ultrabasic and basic rock compositions in the complex multicomponent system required to represent them completely, the patterns of fusion and crystallization described above for the join $2MgO.SiO_2$–$CaO.FeO.SiO_2$ (fig. 2*b*) could occur during certain

petrological processes. The petrological deductions are speculative, because the phase equilibrium relations are tentative in many parts of the systems discussed, and comparison between the synthetic systems and rocks was qualitative only. However, their implications are of sufficient interest to justify their further consideration.

If, in fig. 2*b*, the composition range 10Fo to 20Fo is equated to basalts, and the range 50Fo to 80Fo is equated to picrites and peridotites, then compositions on the liquidus plateau between 20Fo and 50Fo would represent rocks ranging from olivine basalt to picrite (compare figs. 2 and 3). Substituting rock-names for the formulae used earlier, the crystallization and fusion relations derived from fig. 2*b* may be restated thus:

Fusion of crystalline picrite and peridotite. The first liquid developed would be basaltic. As the temperature was raised, the amount of liquid would increase slowly, without much change in composition, until the temperature reached a value such that the liquid passed the threshold of the liquidus plateau. There would then be a rapid increase in the rate of fusion for slight additional temperature increases, with a corresponding change in liquid composition.

Solution of forsteritic olivine crystals in basaltic magma. Basaltic magmas containing suspended forsteritic olivine crystals would be able to dissolve a considerable proportion of the crystals if the temperature rose above that of the plateau threshold.

Crystallization of picritic liquids. A high proportion of the liquid would crystallize in a small temperature interval, and the forsteritic olivine precipitated would change composition only slightly.

The products of the first two processes would be olivine basalt and picritic magmas. Much higher temperatures would be required to produce liquids of peridotitic or dunitic composition. For instance, the liquidus temperature of the projected picrite *P*, containing 61 modal % of olivine, lies about 100° C. above the liquidus plateau on the orthosilicate join (figs. 2 and 3). The third process illustrates the crystallization behaviour of magmas rich in dissolved forsterite. These statements may now be compared with current petrological theories.

Discussion.

'There is general agreement among geologists that basaltic magma is primary' (Turner and Verhoogen, 1951, p. 362). The concept of primary or parent basalts derived from crustal layers of glassy or crystalline basalt (Daly, 1933; Kennedy and Anderson, 1938; Turner and Verhoogen, 1951, p. 363) has played an important role in the evolution of

petrological theory, but such basalts are not always adequate to explain the succession of differentiates produced in a particular province. Bowen (1928) regarded the peridotite substratum as the source of basaltic magmas, and Hess (1938) suggested that primary peridotite magmas could be derived from the same layer. In several recent publications there have been renewed suggestions that primary basalts are derived by the selective fusion of crystalline material, probably peridotite, below the Mohorovičić discontinuity, and the available geophysical evidence appears to be compatible with the suggestion (Green and Poldervaart, 1955; Powers, 1955; Wager, 1956). Additional support is offered by the results of controlled thermal experiments on selected basalts, representative of the major basaltic magma types. These led Yoder and Tilley (1957, p. 159) to conclude, tentatively, that all basalts were themselves the product of the same melting process, although they did not specify the material that melted.

If the selective fusion of peridotite gives rise to basaltic magmas only, which is the opinion of most petrologists, there must be some kind of control in operation that prevents the development of magmas more basic than basalt. The composition of the liquid produced by partial fusion of peridotite will depend upon three main factors: the composition of the crystalline peridotite, the temperature of fusion, and the shape of the liquidus surface in the complex basalt–peridotite system.

The first factor may account in part for the variation in composition between saturated tholeiitic magma types and undersilicated alkaline types (Kennedy, 1933; Green and Poldervaart, 1955; Yoder and Tilley, 1957, p. 159). If there is a limit to the amount of heat available such that the temperature of the magma does not exceed a definite value (Powers, 1955), then the second factor could be the main control. However, the process of partial fusion has occurred frequently (in geological time) and in varied tectonic environments, and it seems remarkable that the temperature should always have risen just high enough to melt out the basaltic fraction. It is more likely that the fusion temperatures have varied from time to time and from place to place, and that the control is effected by the third factor, the shape of the liquidus surface. It has been demonstrated earlier that this could limit the composition of the melted fraction over a considerable temperature interval.

If a range of melting temperatures is admitted, the temperature could occasionally rise high enough to pass the threshold of the plateau on the liquidus surface, if such exists. This would give rise to magmas containing a high proportion of dissolved forsterite. Bowen (1928) believed that

basaltic liquids never contained more than 12–15 % of olivine in solution, but Drever (1956) has presented evidence that picritic magmas containing up to 25 % of dissolved forsterite may be a widespread and important type. The earlier discussion illlustrates how such magmas could develop without the requirement of very high temperatures.

Some of the olivine basalts commonly believed to represent basalt magma plus accumulated olivine could thus represent original magmas. The presence of olivine phenocrysts need not indicate that they accumulated from a parent basaltic magma (Drever and Johnston, 1957; Wyllie, 1958*a*). Resorption and the development of skeletal forms in olivine phenocrysts could be a reflection of the solution and reprecipitation of considerable amounts of olivine in response to minor temperature fluctuations. The degree of fractionation of early olivine precipitates governs the extent to which a basaltic magma can produce acid derivatives. It is important, therefore, to establish more closely how much of the olivine in specific basalts crystallized in place, and how much was separated from a parent basalt elsewhere. The growth properties of olivine make this a difficult task.

The olivines in many olivine-rich rocks are only slightly zoned (Drever, 1956; Drever and Johnston, 1958; Wyllie, 1958*a*). This fact is generally adduced as evidence that they could not have crystallized *in situ* from a homogeneous magma, but it has been shown above that a picritic liquid could precipitate a high proportion of forsteritic olivine with very little change in composition.

A plateau on a liquidus surface like that illustrated in fig. 2*a* frequently implies the presence of a metastable region of liquid immiscibility below the surface. The effect of water vapour under pressure could conceivably lower the liquidus temperatures sufficiently for the surface to intersect such a field of immiscibility. This possibility should not be dismissed out of hand. Drever's (1960) discovery of globules in the non-porphyritic zone of a picrite sheet could indicate the former existence of immiscible liquids.

These remarks are sufficient to indicate that if a plateau is present on the liquidus surface of the basalt–peridotite system, several petrological axioms must be critically re-examined. It is desirable to measure the liquidus and solidus temperatures of a suite of rocks with compositions ranging from basalt to picrite, both dry and under hydrothermal conditions, to see whether a plateau does exist in the natural system. Such measurements are not readily made, because of the high temperatures required, and because of difficulties involved in the interpretation

of quenched liquids rich in olivine. Equipment planned or under construction in this department should cope with the first difficulty, and it is hoped that even with an increase in the proportion of olivine over that present in basalts the original condition of the quenched products can be deduced (cf. Yoder and Tilley, 1956, p. 169).

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A possible explanation of immiscibility in silicate melts.

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Summary. The problem of silicate immiscibility, of petrological and technological interest, is discussed in terms of the structures of silicate crystals and certain phase diagrams. Physical chemical principles are employed to indicate the author's basis for suspecting that certain structures in the crystalline solid are carried over into the melt and are a major contributory cause of silicate immiscibility. These structures appear to be limited to the neso $(SiO_4)^{4-}$, soro $(Si_2O_7)^{6-}$, cyclo $(Si_3O_9)^{6-}$, and ino $(SiO_3)^{2-}$ types of silicate polymers and do not include the more complex phyllo- and tecto-silicate polymers.

THE following discussion is an attempt to approach the phenomenon of immiscibility in silicate and some borate systems from a chemical crystallographic point of view. In general, previous authors (Warren and Pincus, 1940; and Dietzel, 1937) have suggested that an explanation of the phenomenon of immiscible silicate melts may well lie in considerations of electrostatic share potentials and field strengths of the cations involved in such relationships. Their hypothesis appears to be that the attraction of the silicon ion for all available oxygen in the liquid state is matched or outweighed, in certain instances, by the desire of the cations to become properly coordinated by oxygen ions.

In this present paper it is suggested that consideration of the anionic groups may aid an understanding of the occurrence of immiscible regions. It should be noted that, generally, previous authors did not consider the specific sub-systems involved but rather limited themselves to visualizing actions of the two extreme end-members of a large two-component system, e.g. CaO–SiO_2 rather than the real sub-system involved, $CaSiO_3$–SiO_2 (fig. 1). Since in numerous instances intermediate melting compounds are in a eutectic relationship with SiO_2, it appears to be more in accord with structural realities to consider the actual binary sub-systems showing immiscible relationships.

In order to facilitate an understanding of this particular approach a list of most of the major immiscible and many miscible systems with the network formers SiO_2 and B_2O_3 was prepared. Where feasible,

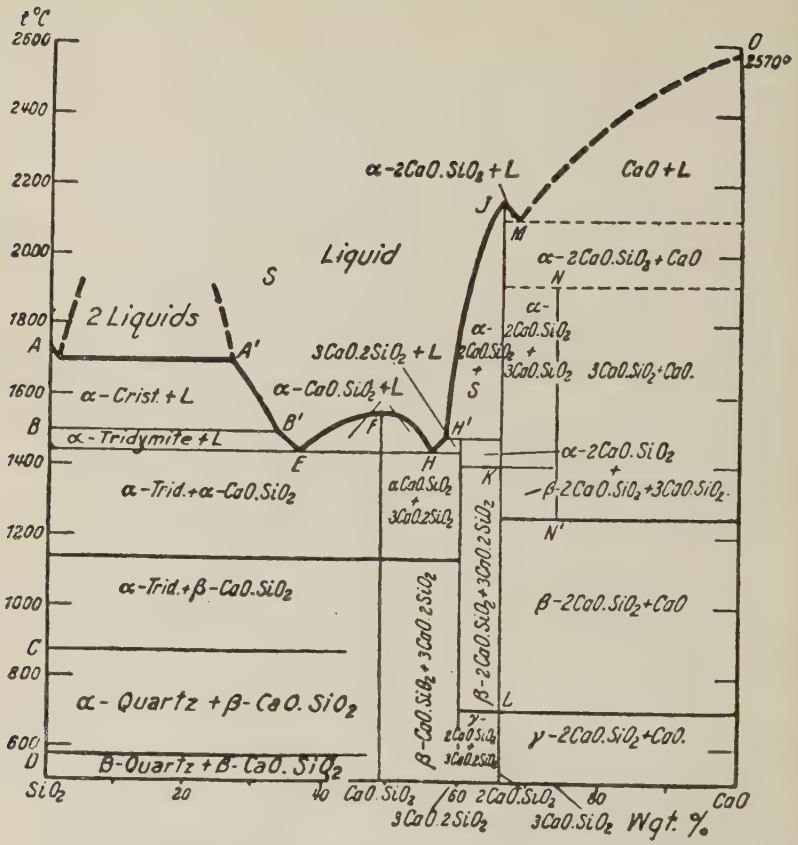

FIG. 1. Binary system silica–calcium oxide, corrected (Rankin and Greig).

systems having a common cation, e.g. Ca^{++}, are listed together, and immiscible systems are shown in heavy type:

$CaSiO_3$–SiO_2	**Mg_2SiO_4–SiO_2**	$Li_2Si_2O_5$–SiO_2
$CaMgSi_2O_6$–SiO_2	**$Mg_2B_2O_5$–B_2O_3**	$Li_2B_{10}O_{16}$–B_2O_3
$CaAl_2Si_2O_8$–SiO_2	**MnO–Mn_2SiO_4–$MnSiO_3$–SiO_2**	$K_2Si_4O_9$–SiO_2
CaB_2O_4–B_2O_3	MnB_6O_{10}–B_2O_3	$K_2Al_2Si_6O_{13}$–SiO_2
PbB_4O_7–B_2O_3	**$SrSiO_3$–SiO_2**	$K_2B_{10}O_{16}$–B_2O_3
$PbSiO_3$–SiO_2	$BaSi_2O_5$–SiO_2	B_2O_3–SiO_2
Fe_2SiO_4–SiO_2	$Na_2Si_2O_5$–SiO_2	Al_2O_3–SiO_2
Zn_2SiO_4–SiO_2	$Na_2B_8O_{13}$–B_2O_3	GeO_2–SiO_2

From this list it will be observed that the cations Pb^{++}, Mn^{++}, and Ca^{++} form a miscible as well as an immiscible system with such similar network formers as SiO_2 and B_2O_3.

The field strength of an ion is $Z/(Ra + Rx)^2$, where Z is its valence and Ra is the radius of the anion, Rx of the cation. It has been suggested by previous authors that cations with high field strength lead to immiscibility, but Mn^{++} with a field strength as high as 0·48 does not form an immiscible relationship with B_2O_3 while Pb^{++} with a field strength of only 0·34 does; further, the oxides of boron, germanium, and aluminium with ionic field strengths of 1·65, 1·75, and 0·84 respectively, do not show immiscible relationships with the network former SiO_2.

The electrostatic share potential is defined as $q = Z/CN$, where CN is the coordination number of the ion, and it has been suggested that a high share potential leads to immiscibility. When in sixfold coordination, Ca^{++}, Mg^{++}, and Pb^{++} have a similar electrostatic share potential of 0·333, but again immiscibility with a network former does not always result. For example, MnO-B_2O_3 shows no immiscibility while PbO–B_2O_3 does; again B^{+++}, Ge^{+++}, and Al^{+++} with share potentials of 1, 1, and 0·50 to 0·75 show no immiscibility.

To obtain a more consistent picture of immiscibility, an analysis of the significance of the morphology of the liquidus would be helpful. In the analysis of a liquidus slope, which usually indicates the effect of the colligative property called freezing-point lowering (ΔT_f), it is helpful to consider the equation $\Delta T_f = RT_fT_l\, a\, \gamma\Delta H_f$, where ΔH_f is the latent heat of fusion of the primary phase, R the molar gas constant, T_l the liquidus temperature of the primary phase region, T_f the melting-point of the pure primary phase, a the activity of a particular component of a solution, and γ the activity coefficient.

The presence of a liquid miscibility gap, characterized by a horizontal discontinuity in the liquidus curve, indicates a region where a positive deviation from Raoult's law $P_a/P_a^{\circ} = a/\gamma$ exists (P_a is the partial vapour pressure of constituent a, P_a° the vapour pressure of the pure constituent a). The interpretation of such a liquidus shape has usually been that association, resulting from dipole formation, has taken place. In general such dipoles are due to structural distortions and orientation of specific units in the liquid in response to some field of force. It is known that the magnitude of the induced dipole is related not only to the polarizability of the unit but also to the concentration of such structures in the liquid and to the magnitude of the forces inducing this phenomenon. The relationships of some of the above factors are given by the Debye equation:

$$P = (4\pi nM/3\rho)(\alpha_0 + u^2/3KT),$$

where P is the polarization of the structure, n the number of polarizable structures per unit volume, M the mass of the structure, ρ the density of the structure, α_0 the distortion effect factor, $u^2/3KT$ the orientation effect factor (u, being the dipole moment, $= \alpha F$, where α is the polarizability and F is the intensity of applied field), and K is Boltzman's constant.

At this point one ought to consider what types of liquid structures are associating and thus causing a decrease in ΔT_f, and this involves some general considerations concerning the structure of silicate melts, a matter on which there is at present no general agreement. In a later paper we hope to discuss our viewpoint in more detail and to present new experimental data.

Structural considerations concerning silicate melts. In general, the fusion of silicates is accompanied by negligible increases in volume. If one assumes that the volume of the quenched glass is not very different from that of the liquid, the slight change in volume between a solid and its melt is exemplified by the following data from Huckel (1951), where the volumes of some glasses and crystals are presented, extrapolated to absolute zero:

	Na_2SiO_3	$Na_2Si_2O_5$	$CaSiO_3$	$BaSiO_3$
Crystal	46·7	73·0	40·0	48·2
Glass	47·7	73·1	40·0	48·3

These and other data considered below suggest that the arrangement of structural units in a liquid, in the neighbourhood of the liquidus at least, must be somewhat related to that in the crystalline solid from which it originated. Further, the latent heat of fusion is much smaller (by a factor of 30 to 40) than the latent heat of vaporization. It would appear from this that the forces between structural units decrease only very slightly in the process of melting, in agreement with the observation that the volume increase is slight. Again, the specific heat of condensed bodies is only very slightly effected by melting, being somewhat greater just above the melting-point than just below it. This could well indicate that the character of thermal motion near the point of stable nucleation remains fundamentally the same as in crystalline materials, small vibratory movements about ionic equilibrium positions. This viewpoint is in agreement with the preceding since the slight increase of distance between structural entities cannot effect materially the binding forces nor the character of their vibratory motion.

Simple thermodynamic calculations, based on the fundamental equations $\Delta G = \Delta H_f - T\Delta S$ and $\Delta S = \Delta H_f/T$ (since $\Delta G = 0$ under

equilibrium conditions at constant pressure), indicate that the change in entropy for silicates is slight for transitions across the liquidus (ΔG is the change in free energy, ΔH_f the heat of fusion, T the temperature in °K., ΔS the change in entropy). Again this would indicate that the change in the degree of structural order or disorder on melting is small.

Consideration of the relation of thermal expansion and composition to the structure of glasses (Blau, 1951) tends to indicate that the silicate anionic group configuration in glass is reminiscent of that of the crystalline solid; and thermodynamic evaluation of the silicate system (de Wys, 1955) $CaAl_2Si_2O_8$–$Ca_2MgSi_2O_7$ tends to support the above viewpoint. Again, Lark-Horowitz and Miller (1936) found a similar X-ray diffraction pattern for the melt and the crystal phase, while Randall, Rooksby, and Cooper (1930) investigated wollastonite and borax glasses which showed the X-ray diffraction interference bands of $CaSiO_3$ and $Na_2O.2B_2O_3$ in broad, indistinct rings. In the literature one may readily find illustrations where electroconductivity measurements (Bockris, 1948) and viscosity (Preston, 1942) data tend to support the above viewpoint in respect to the structure of silicate melts.

It would appear that an ion-pair with a small negative electrostatic potential would suffer greater separation than an ion pair with a larger negative electrostatic potential. In considering this potential energy per pair of ions in a crystalline structure, the energy, U, may be related to the coulomb ionic effect and the repulsive potential. The increase of lattice stability due to polarization also comes into consideration. A formula simplifying some of the above relationships may be written as:

$$U = (AZ_1Z_2e^2/r^2)+(B/r^n)-(ZeU_p/r^2),$$

where the first term is the Coulomb potential, the second the repulsive potential, and the last the effect of the polarization, with $U_p = \alpha F$ as was indicated by the Debye equation. Obviously then, besides the effect of electrostatic share potential, the polarizing power and polarizability of the ions concerned must be considered. Goldschmidt (1926) has proposed using the quantity Ze/r^2 as a measure of ionic polarizing power. Polarizability of an anion, however, appears to increase with ionic radius. Finally, the presence of a resonance phenomenon apparently increases significantly the stability of an ion-pair. Since the radius of Si^{4+} is considerably smaller than those of the other ions considered (Mg, Li, Zn, Fe, Mn, Na, Ca, Sr, Pb, K, Ba) and its valence is higher, it is to be expected that the Coulomb term would indicate greater ion-pair stability for a Si–O configuration than any of the other cation–O bonds.

The electrostatic share potentials, q, for some of the ions are included in table I. Clearly the potential for Si–O is far greater than those for the other ions listed; this again indicates a greater stability for the Si–O pair than for the other cation–O bonds. When these cations are reduced to 'rambling' units in a melt it seems likely that the stability differences will be even more pronounced.

The polarizing powers, Ze/R^2, of various cations, after Goldschmidt (1926), are also included in table I. Again, the value for Si^{4+} is much

TABLE I. Physical constants for various ions. C.N., coordination number; q, electrostatic share potential; Ze/R^2, polarizing power; e.n.d., electronegativity difference between the cation and oxygen.

	Ca^{2+}	Mg^{2+}	Mn^{2+}	Pb^{2+}	Fe^{2+}	Zn^{2+}	Sr^{2+}	Ba^{2+}	Na^{+}	K^{+}	Li^{+}	Si^{4+}
C.N.	8 or 6	6 or 4	6	6	6	4	8	8	8	8 or 12	6	4
q	0·25–0·33	0·33–0·5	0·33	0·33	0·33	0·50	0·25	0·25	0·125	0·125–0·08	—	1·00
Ze/R^2	1·78	3·27	—	—	—	—	1·24	0·98	1·04	0·57	1·64	26·30
e.n.d.	2·5	2·3	—	2·9	—	2·0	2·5	2·6	2·6	2·7	2·5	1·7

higher than for the other cations, suggesting that the Si O pair should be more stable by virtue of the polarization effect term of the potential energy of ion pairs.

It is known that when the electronegativity difference between two atoms is small, both ionic and covalent types of bonding may contribute to the resultant ion-pair configurations, and resonance between the two types of bonds is superimposed on the resonance associated with the normal homopolar bond and thus increases the bond energy. The electronegativity differences between the various cations and oxygen (table I) indicate that the resonance contribution to the Si–O bond is likely to be more significant than to the other cation -O bonds.

From all of the considerations stated above, it would appear that on the basis of chemical crystallographic theory and other data, the particular predominant type of silicate anionic structure would tend to be preserved in the liquid state in preference to any other cation-oxygen grouping. In general, then, all of the considerations taken into account seem to indicate that the liquid, at least immediately above the liquidus, shows some type of a structural memory of the crystalline state and that such a structural resemblance would be especially pronounced in silicate melts.

General hypothesis of immiscibility. With this in mind, it appeared fruitful to reconsider some of the systems characterized by the presence or absence of a miscibility gap. Considerations of the significantly lower bond strength of the cations and the observation that a particular cation

could partake in an immiscible as well as a miscible relationship with the same network former, tended to emphasize the need for recognizing the role enacted by the anionic structures.

Analyses of the immiscible systems in terms of the anionic groups indicate that only those compounds that have the following type of complexes enter into an immiscible relationship with a framework-type liquid such as SiO_2: neso, $(SiO_4)^4$; soro, $(Si_2O_7)^{6-}$; cyclo, $(Si_3O_9)^{6-}$, $(Si_4O_{12})^{8-}$, and $(Si_6O_{18})^{12-}$; ino, $(SiO_3)^{2-}$ or $(Si_4O_{12})^{6-}$.

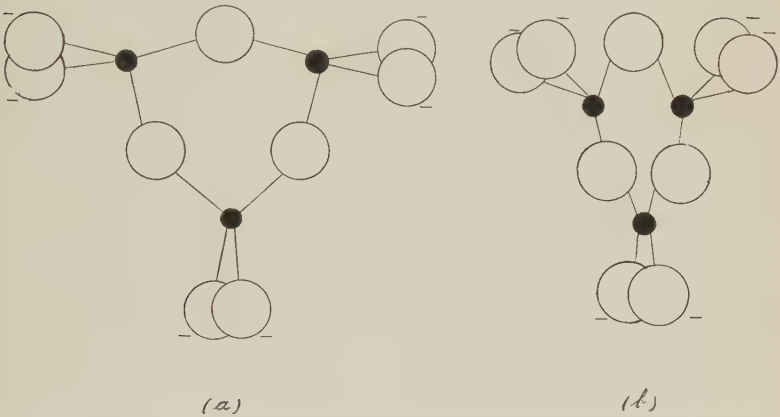

FIG. 2. Diagram showing a non-deformed (*a*) and deformed (*b*) ionic group $Si_3O_9^{6-}$.

The miscible systems showed only phyllo- or tecto-types of complexes such as: phyllo, $(Si_2O_5)^{2-}$; and tecto, $(Al_2Si_6O_{12})^{2-}$, $(Al_2Si_2O_8)^{2-}$, and SiO_2 (the $(AlO_4)^{5-}$ complex is considered simply a part of the SiO_2 network).

It would appear, therefore, that only those complexes with two or more non-bridging polarizable oxygen ions per network-forming ion tend to pronounced associative phenomena in a binary solution. As an example the behaviour of the silicate complex $Si_3O_9^{6-}$, which if the dominant structure in a particular crystalline compound would be present in the liquid, may be visualized in a compressive or non-compressive force field as shown in fig. 2.

From this schematic diagram it would appear that on deformation of such a complex containing six non-bridging oxygen ions a structural dipole would be formed with resultant associative effects. Considering, for example, the system $CaSiO_3$–SiO_2 rather than the general binary CaO–SiO_2 it becomes evident that in the crystalline mixture, below the

eutectic horizontal, units with cyclo-structures of the type $Si_3O_9^{6-}$ are in equilibrium with the tecto-type SiO_2 compound. It would appear that if such ring structures were caught, in a state of liquid equilibrium, inside a compressing, thermally oscillating SiO_2 framework, the existence of which has been reasonably well established, the formation of induced dipoles with resultant association and thus positive deviation from Raoult's Law would result. In essence this is what we would like to suggest as a possible explanation of the immiscibility observed.

In the system $CaSiO_3$–SiO_2 a liquid corresponding to the composition on the high SiO_2 side of the two-liquid region shown in fig. 1 was apparently so viscous that it pulled away from the crucible walls on cooling and remained as a rigid amorphous cylinder. A liquid of the composition on the high $CaSiO_3$ side, however, formed a more fluid spheroid at the bottom of the crucible. It would appear that some significant structural difference may thus exist between the two. One may speculate, with Warren, that on the SiO_2 side, the SiO_2 network remains sufficiently intact to withstand, to a large extent, the collapsing thermal forces. An increase of the number of $Si_3O_9^{6-}$ complexes and their orientability would result, as is indicated by Debye's formula, in an increased dipolar strength, which is represented by the higher temperatures needed to overcome the increased association effects. On the $CaSiO_3$ side, the framework, and thus the intensity of the applied field as indicated by the Debye equation, is apparently rapidly breaking down so that even a continued increase of cyclo complexes is insufficient to preserve continued immiscibility. The downward slope of the line separating the two liquid and the one liquid phase region, as shown in fig. 1, is the result. The peak of the miscibility gap apparently represents the combined optimum effects of network rigidity and $Si_3O_9^{6-}$ concentration.

A similar point of view may be readily developed for borate compounds forming a miscible or immiscible relationship with B_2O_3.

We now seem to have an explanation of the apparent contradiction observed when only cations are considered. For example, $CaSiO_3$ is a cyclo-compound, $CaMgSi_2O_6$ and CaB_2O_4, also having an immiscible relationship with SiO_2, are known to be ino types of compounds while, in contrast, $CaAl_2Si_2O_8$ is a tecto type of compound, which would explain why it forms a miscible system with SiO_2.

Greig (1927) stated that: 'The similarity in chemical behaviour of calcium, strontium and barium, together with the fact that the liquidus of silica rises very steeply from the eutectic tridymite–$BaSi_2O_5$ suggested that baria, like magnesia, lime and strontia would be only partially

miscible with silica.' It is, of course, well known that the system BaO–SiO_2 does not show any miscibility gap. In considering the actual sub-system $BaSi_2O_5$–SiO_2 no such a gap would be expected according to the point of view suggested in this paper since $BaSi_2O_5$ is a phyllo-silicate and thus has less than two non-bridging oxygens per Si ion.

Conclusions. On the basis of crystal chemical considerations the author suggests that the structure of the anionic groups appears to be the main determinant of the occurrence or absence of immiscibility although consideration of field strength and electro-static share potential may have some practical validity.

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Secondary minerals of the Tertiary basalts, Barrington, New South Wales.

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Summary. Secondary minerals described from Tertiary amygdaloidal basalts in the Hunter Springs area, Barrington, New South Wales, are regarded as having been deposited from cold solutions some considerable time after consolidation of the basalts. The constituents in the solutions were evidently derived from the basalts by the action of circulating meteoric waters rather than by deuteric activity.

THE basalts that characterize the Mt. Royal and Barrington Highlands, about 50 miles north-west of Newcastle, New South Wales, are Tertiary in age. According to Browne (1933) they belong to the Newer Basalts and were poured out most probably during early Pliocene times, but David (1950) regards them as belonging to the Older Basalts and Oligocene in age. However, their exact age is immaterial as far as this paper is concerned.

Browne describes the flows as follows: 'The successive flows of basalt are indicated by flat topped terraced hills . . . the terracing . . . being due to the erosion of alternately amygdaloidal and massive layers of basalt.' For the most part, the flows are between 15 and 20 feet thick, and have a total thickness of approximately 700 feet according to Sussmilch (1940, p. 304), although Brown's estimate (1933, p. 37) is 1 500 feet.

The basalts that overlie unconformably the truncated ends of the folded Carboniferous and Devonian sediments contain abundant secondary minerals.

The samples were collected from Black Cutting along the road from Moonan Flat to Tomalla in the valley of the headwater of the Hunter, the 'Escarpment', and Tubrabucca Falls. Fig. 1 indicates the approximate location of these places.

There are two types of basalt, which form alternating layers: a massive basalt with few vesicles, and a highly vesicular basalt with partially and completely filled vesicles.

The massive basalt is largely porphyritic with phenocrysts of olivine

averaging 1·0 to 1·5 mm. in length and constituting 20 % of the rock. The phenocrysts are set in an intergranular groundmass of small laths of labradorite averaging 0·5 mm. long and granular pyroxene with average grain size of 0·5 mm. The labradorite constitutes about 40 % of the rock and the pyroxene about 30 %. Scattered throughout the rock are granules of magnetite and ilmenite and minute needles of apatite, all in

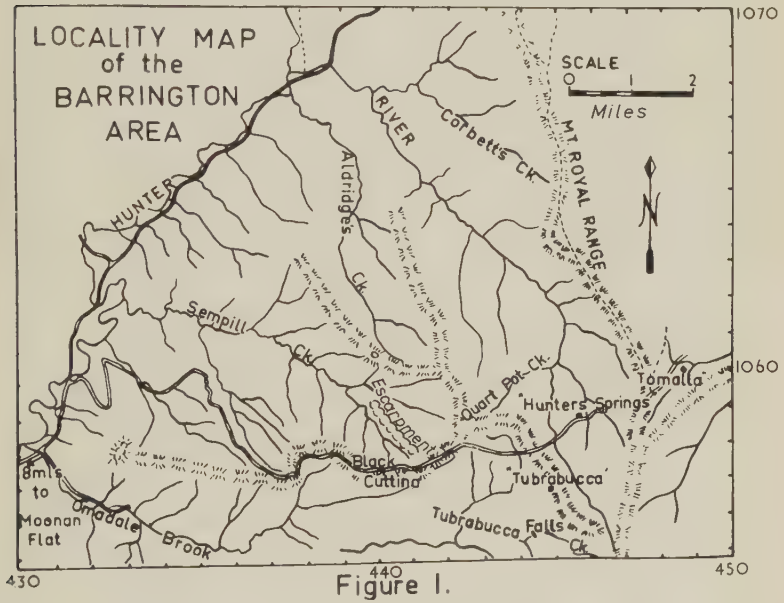


Figure 1.

subordinate amounts. In some of the basalts the olivine shows incipient alteration to chlorite along the cracks and around the rims while in the majority chlorite, in varying amounts, is intersertal. Vesicles are few in number and more regularly ovoid than those in the amygdaloidal type. Their infillings are discussed below.

The amygdaloidal basalt shows various degrees of weathering in contrast to the fresh massive type. Megascopically, the rock has taken on a brown colour and crumbly texture and has the appearance of a very much altered rock. Microscopic investigation reveals that the olivine and augite have altered to limonite with some granules of magnetite, still relatively fresh, interspersed, and the plagioclase has altered to albite. This basalt is extremely amygdaloidal. The vesicles and their infillings are described below. Much of the amygdaloidal basalt is of a blocky

type in which the blocks vary from 5 to 20 cm. in diameter. Some flows of this basalt reveal distinct elliptically shaped volcanic-bomb-like masses.

Nature of the vesicles and their infillings. The vesicles vary greatly in abundance and size. In the massive type they are few while in the scoriaceous material they are abundant. In size they vary from less than 1 mm. to 20 mm. and in shape from small ovoid cavities to larger irregular openings. One example showed vesicles elongated in the direction of flow and subsequently partly filled with horizontal layers of clay.

The minerals that fill the vesicles are chabazite, natrolite, montmorillonite, montmorillonite interlayered with illite, chalcedony, manganite, and calcite. They form either singly in some vesicles or in a variety of combinations as indicated in fig. 2.

The order of deposition of the minerals can only be as follows: manganite, montmorillonite interlayered with illite, montmorillonite, chabazite, natrolite, a second generation of manganite, and, finally, chalcedony and calcite. The last two also commonly infill veins that cut across the flows.

The vesicles in the massive type of lava are usually filled with one of the following combinations: chabazite; chabazite lining the vesicle and natrolite occurring in the centre; chalcedony; or radiating natrolite lining the vesicles and chalcedony filling the interior space.

Secondary minerals.

Montmorillonite occurs as two distinct forms:

As bands of clay that are cream coloured at the top grading down to mid-green with dark green at the base. X-ray analysis proved the clay to be montmorillonite and revealed practically no difference between the three varieties. There was only a very slight shift in each line of the powder photograph, and no marked difference in refractive index (n 1·499) was detected.

As a cherry red variety (like hematite), which is recorded separately from the first type of montmorillonite because it occurs in distinct layers in the vesicles and not as though it is an iron stained variety of the first type. The mineral did not react readily to qualitative tests for iron but chemical analysis carried out by G. T. See of the University of New South Wales revealed 5·10 % Fe_2O_3.

Much of the material occurs as a powdery lining to the vesicles, but often the structures assumed are stalactitic and nodular. X-ray analysis

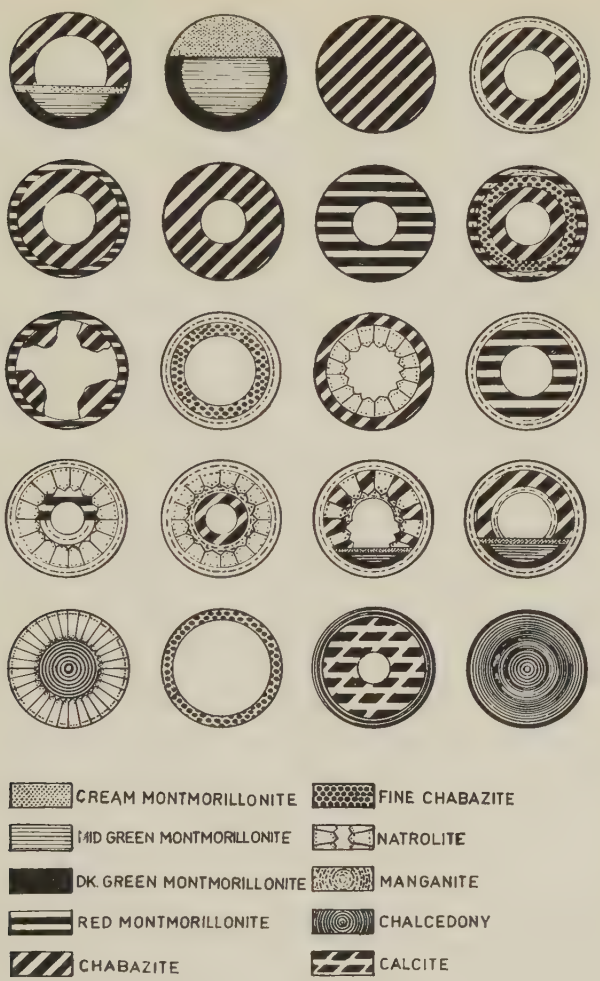


FIG. 2. Illustrates diagrammatically the combinations and arrangements of the secondary minerals in the vesicles of the highly vesicular basalt.

revealed that the mineral is montmorillonite (about 80 %) interlayered with illite (about 20 %).

Chabazite varies in form from a simple rhombohedron to a more complex crystal consisting of the rhombohedron and other forms. The crystals range in size from microscopic dimensions to about 5 mm. in diameter. In some vesicles the chabazite occurs as a thin film.

Irrespective of the form, the mean refractive index is 1·490 and the sign optically negative.

Natrolite occurs as acicular crystals under 5 mm. long and as slender, hair-like crystals either surmounting other minerals or in separate radiating groups. One vesicle broken open revealed a lining of chabazite and enmeshed, doubly terminated fibres of natrolite. Natrolite occurs also in veins and cavities other than the vesicles in the basalts.

Chalcedony occurs concentrically arranged in the vesicle like the clay (montmorillonite). It shows aggregate polarization, and the refractive index and water content are more those of common opal, being n 1·488, H. 6, H_2O 13·23 % for the white chalcedony, and n 1·489, H. 6½ H_2O 9·14 % for the cream. The water content recorded was that driven off after prolonged heating at red heat and is high relative to its refractive index. The high water content is due to some vesicles containing silica gel. The H_2O of newly exposed vesicles was observed to be very variable. With exposure to air the gel soon dried out.

Calcite is not nearly as abundant as associated chabazite and chalcedony, with which it is closely related in time of deposition. It is the transparent variety.

Manganite occurs as a black, powdery lining to some vesicles, or dusting the infillings of other vesicles; it also occurs in veins. Its chemical composition was derived by qualitative chemical tests but could not be confirmed by X-ray analysis owing to the difficulty of collecting sufficient material.

Origin of the secondary minerals.

The question arises whether the secondary minerals were deposited from deuteric solutions or from extraneous hydrothermal solutions of meteoric origin, or of later igneous origin.

Possibility of origin from deuteric solutions. The vesicles in Tertiary amygdaloidal basalts from other localities in the Barrington district are filled with chabazite, natrolite, montmorillonite, and calcite. The olivine-free Tertiary basalts that outcrop at Ardglen about 50 miles to the west have similar amygdules of chabazite, natrolite, montmorillonite of both varieties, and manganite. These examples indicate that such constituents are prevalent in basalts of this age. They point to a deuteric origin, but the associated natrolite, chalcedony, and manganite in the Barrington localities are found not only within the vesicles, but also infilling joints that were no doubt developed long after consolidation of the flow.

The highly vesicular lava indicates rather rapid consolidation so that all magmatic liquors would be expected to have crystallized and left none to move through the rock as deuteric solutions. There would thus be insufficient to satisfy the requirements of the large quantities of amygdaloidal secondary minerals observed. The recent scoriaceous basalts of the Hawaiian Islands are of comparable character. These are completely consolidated and intensely vesiculated, the vesicles being devoid of infillings except for an occasional thin layer of sublimate.

Throughout the literature on the Hawaiian lavas little mention is made of vesicle infillings. Macdonald (1949) writes: 'Pololu Volcanic Series: Olivine basalt pahoehoe, thin bedded, much weathered, reddish-brown and soft, many joint surfaces coated with a purplish-black submetallic substance, probably manganese oxide. Many vesicles partly filled with calcite and probably zeolites.'

This prompted one of us (B. N.) to inquire from the Hawaiian Volcano Observatory (U.S. Geological Survey) whether the bulk of the vesicles in the Hawaiian flows were filled and, if so, whether the rock was fresh or weathered; also the depth in the volcanic pile at which infillings in the vesicles become prevalent, and the age of these lavas.

Mr. G. D. Fraser (priv. comm.) informed us that the primitive undifferentiated basalts contain about 30 % void space and abundant vesicles but no zeolites at all, regardless of age and depth of burial. However, near fumarolic areas clay minerals, sulphates, and opal are common in the altered rock and in the vesicles, zeolites being rare or absent. In some areas, where zeolites have been found, the most common host rocks are unusually undersaturated or differentiated.

Similar information was sought for the geologically young lavas of New Zealand and New Guinea. Mr. D. Kear of the Geological Survey of the Dept. Sci. Indust. Research in New Zealand indicated that many of the Auckland bassalts (Holocene to Upper Pleistocene in age) are highly vesicular. A few of the vesicles are reputedly filled with calcite but in general the vesicles are void of minerals. The vesicles in some of the older weathered lavas are sometimes coated with a mere white film that may prove to be zeolitic. Mr. Kear also remarked that the Upper Pleistocene and Recent basalt flows on Samoa are unweathered, unaltered by thermal solutions, and have no vesicle infillings.

Dr. G. Baker of the Mineragraphic Investigations Section, Commonwealth Sci. Indust. Res. Organ., Melbourne, sent similar information on lavas in New Guinea. Baker (1946) indicated that the vesicles in lavas from the Goropu volcanic eruptions of December 1943 to August 1944

are not infilled and the rocks show no hydrothermal alteration. Again, Baker (1948) pointed out that any vesicles in young basalt from Oiava-ai on Goodenough Island and in andesites from the Amphlett Group are not infilled. Similarly, the volcanic rocks (Quaternary to Recent) of Mt. Bogana, Bougainville Island, Solomon Islands (Baker, 1949), do not have their vesicles infilled and are not hydrothermally altered to any extent. However, the older Aitape lavas in the Bismarck Archipelago, which are Lower Miocene in age, have many infilled vesicles (Baker, 1954).

The data point to the fact that when lavas are first consolidated, and for some considerable time thereafter, their vesicles remain unfilled. Both Fraser and Baker (priv. comm.) suggest that fumarolic action may play some part locally in the alteration of lavas and in the infilling of some of their vesicles. Such action, no doubt, would be limited in geographic distribution. Similar infillings of vesicles are fairly universally distributed in the Tertiary basalts of eastern Australia and do not occur in isolated patches, as one would expect, as the result of fumarolic effects. Evidently the infillings post-dated consolidation and were thus not a direct result of deposition from deuteric solutions, so that extraneous secondary solutions must have been responsible.

Possibility of origin from extraneous secondary solutions. Extraneous secondary solutions could be either of magmatic origin, that is, emanating from an igneous intrusion injected some time after the consolidation of the basalts, or of meteoric origin, from circulating subterranean solutions.

As there has been no post-basalt igneous intrusion of a magnitude to produce such solutions the possibility of the solutions being magmatic could not hold, hence the only possibility is meteoric. The only igneous rock type in the region is basalt, hence such solutions must result from the action of meteoric waters percolating through the basalt, dissolving some of its constituents and redepositing them in vesicles and joint planes. The nature of the alteration of the original rock suggests the possibility that products of this type of alteration gave rise to the secondary minerals listed in tables I and II.

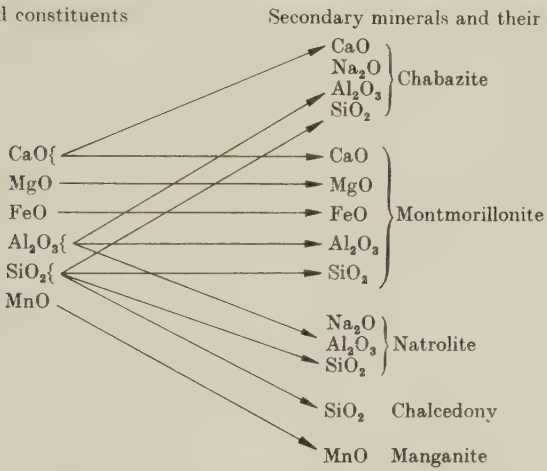
All of the released constituents listed in table I are necessary for the formation of the majority of the newly formed minerals of secondary origin, as is shown schematically in table II.

Although the decomposition of the basalt could release the constituents needed for the mineral infillings of the vesicles in the Hunter Springs localities at Barrington and in other localities, it is only a

TABLE I. Suggested alterations, and constituents released thereby.

Original minerals in fresh basalt	Constituents of minerals	Present minerals in altered basalt	Constituents of minerals	Constituents released during alteration
Olivine	MgO, FeO, MnO, SiO_2	Limonite	FeO	MgO, MnO, SiO_2
Augite	MgO, FeO, MnO, CaO, Al_2O_3, SiO_2	Limonite	FeO	MgO, MnO, CaO, Al_2O_3, SiO_2
Labradorite	CaO, Na_2O, Al_2O_3	Albite	Na_2O, Al_2O_3, SiO_2	CaO

TABLE II. Scheme of formation of secondary minerals.



Note: Na_2O would be released if any of the feldspar (labradorite or albite) is kaolinized.

localized feature and does not explain the infillings in the fresh basalt. However, it is not improbable that downward percolating solutions containing the constituents from weathered basalt at a higher level could affect the fresher and apparently unaltered material. Evidence of this was seen in the traces of solution channels, now filled with secondary minerals, that extend downwards from the weathered section of the rock through the vesiculated area.

Temperature of the secondary solutions. Walker (1951), when discussing the distribution of zeolites, especially chabazite, in the Garron Plateau Area, County Antrim, called upon the agency of hot water solutions to explain the observed distribution of the different habits of that mineral. He did not consider the possibility of cold water solutions, citing only

the generally accepted opinion of other workers in the field, namely that zeolites normally form above 100° C. He deals with the possible sources of heat or mechanisms for the production of heat. One suggestion put forward, but not accepted for the Garron basalts, was that the heat was supplied by the lavas themselves, that is, possibly due to the progressive accumulation of heat in the lava pile by a succession of small additions from each flow erupted. In theory this may seem feasible but in practice and from studies of the recent lavas, it does not happen. Walker finally appealed to the self-generation of heat in the lava pile during zeolitization of the feldspars and hydration of the olivines and pyroxenes. However, such a theory may not be tenable because many of the basalts under discussion are too fresh. For example, the massive basalts from Barrington and the Ardglen basalts were little weathered and show little sign of having been affected by hydrothermal solutions. This fact is borne out by the freshness of the minerals observed in thin sections. The only mineral affected is olivine, as indicated earlier. Secondary chlorite also appears interstitially.

It was reported locally that deposition of a white mineral (probably chalcedony, perhaps with some calcite) and a red mineral (no doubt montmorillonite interlayered with illite) in cavities in the basalts near Tubrabucca Falls from the stream water, which flows over the basalt and has a temperature of about 5° C., had been observed.

More evidence indicating continued deposition of these minerals from cold solutions is provided by the finding of cold solutions actually in the cavities of parts of freshly broken massive basalt. It was impracticable to sample these solutions in the field because the precise position of the containing vesicles could not be detected before the rock was broken open. Upon breaking the rock, the solution immediately trickled over its surface and was lost. However, some of the rock was taken back to the laboratory. Filter paper was specially treated by washing with dilute hydrochloric acid to free it of any impurities. As soon as the specimen was broken and a vesicle containing solution was revealed, the solution was mopped up by the paper. The constituents of the solution held in the paper were then converted to soluble chlorides by treatment with dilute hydrochloric acid. Flame photometry revealed no trace of sodium while qualitative spot tests revealed no trace of calcium, magnesium, iron, aluminium, or silicon. Although the tests used are normally sensitive, the abundances of the salts in solution were evidently too low to reveal even a trace.

The solution-bearing vesicles were lined with a thin layer of a zeolite,

possibly chabazite. This was spotted with small mammillary 'blebs' of chalcedony about 3 mm. in diameter. Some vesicles contained a thin layer of banded dark green montmorillonite.

Additional evidence that these solutions act in the cold is provided by the appearance of a damp rim surrounding vesicles completely filled with chalcedony or with natrolite and chalcedony or with clay. When the rock was freshly broken the original rim was about 2 mm. wide and completely surrounded the filled vesicle. Within 24 hours the width of the rim had expanded to 4 mm. due to surface effects. A piece of rock containing these damp rims was placed in an oven at 105° C. for 6 hours. The rim dried out, but it left a yellowish stain indicating that something more than water was present. The constituents in the solution have not yet been determined.

The problem delineates itself thus: On the one hand there are reports in the literature of hot water solutions being responsible for the deposition and habit distribution of zeolites, while on the other hand there are the actually observed vesicles filled with cold water in contact with chalcedony and montmorillonite, which presumably were deposited from it. The authors have not as yet proved that this cold-water solution was always cold, or that it is capable of further deposition or that it is in any way connected with the more prolific and varied deposition of minerals present in the more vesicular and weathered basalt.

A more fundamental problem that applies to the deposition of all minerals from solution has yet to be solved, and this is the cause and mechanism of precipitation. The commonly accepted possible causes of precipitation appear to be: Reaction of the solution with the wall of the vesicle, reaction of the solution with a previous sublimate either by using it as a nucleus or by actual chemical reaction, slow cooling of a saturated solution, and reaction of hot ascending solutions with descending meteoric solutions.

By way of actual evidence the authors note: that the large and perfectly formed crystals of chabazite tend to favour slow crystallization from an aqueous solution with no marked evidence of co-precipitation; that the radial growth of natrolite crystals around an unidentifiable foreign nucleus indicates slow crystallization; that the red montmorillonite and chalcedony commonly show colloform texture; and that a recognizable, if imperfectly understood, sequence of deposition is apparent, with strictly localized deposition of some minerals or mineral associations.

The first, second, and fourth of these points indicate that the secondary

minerals were precipitated from different solutions. For example, chabazite was deposited from one solution, natrolite from another different solution, and so on. Such different solutions are necessary to explain non-contamination by overlap of crystallization during what must have been a considerably long time. Even when chabazite and natrolite grow side by side they are not structurally intermingled.

The second point indicates the activity and effect of nucleation on the crystallization of natrolite.

The colloform texture of red montmorillonite and chalcedony seems to indicate deposition from colloidal solution, but Krauskopf (1956) contends that silica is transported in true solution in the form of the monosilicic acid, H_4SiO_4, and not as a colloidal solution. He does indicate, however, that over a period of time the true solution is transformed into a colloidal solution. Such a transformation possibly occurred in the vesicles or in the veins or both. The deposition of concentrically layered chalcedony followed. Similar effects may have caused deposition of the red montmorillonite.

The perfection of form of some of the individual crystal species, together with the size and arrangement of the clusters of crystals in an otherwise empty vesicle, seem to indicate slow crystallization from a cold yet saturated solution. These solutions are considered to be still actively depositing mineral matter.

Conclusions.

This study of the secondary minerals in selected examples of Tertiary basalts in New South Wales was conducted with a view to solving some of the physico-chemical problems associated with the movement of secondary solutions through already consolidated lavas. Little success attended considerations of the problems relating to the composition, concentration, rate of movement, and causes of precipitation of secondary mineral matter in the vesicles and joint planes of these basalts, but the following conclusions have been drawn from observations in the field and laboratory: The solutions depositing the secondary minerals were evidently not deuteric but extraneous, namely, percolating meteoric waters. The constituents in the solutions were evidently derived during processes of weathering of the basalts. And the secondary minerals were deposited from cold solutions. This process is still taking place in the Barrington area at a temperature of approximately 5° C.

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A method for quantitative mineralogical analysis by X-ray powder diffraction.

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[Read 5 November 1959.]

Summary. A method of quantitative analysis by photometry of X-ray powder diffraction patterns is described. Co-$K\alpha$ radiation is used and absorption difficulties are overcome by using thin diluted specimens containing an internal standard. An arbitrary universal intensity scale has been established and the values for the stronger lines of a number of minerals are given. Within individual patterns these are consistent with published data obtained by counter diffractometry.

X-RAY diffraction has been applied to quantitative determinations, by comparing the intensities of the diffraction maxima from an internal standard with those of the material to be determined. Both photometric (Hellman and Jackson, 1943; Jarvis, Dragsdorf, and Ellis, 1957) and counter diffractometer (Gross and Martin, 1944; Phillippe and White, 1950) methods have been used.

Many of the primary rock minerals were formed at elevated temperatures and pressures, and are not stable when exposed to the various agencies of subaerial weathering. The processes involved in their alteration to form the more stable secondary minerals characteristic of soils comprise a complex mixture of physical and chemical reactions (Keller, 1957), the course and products of which vary with a number of factors, such as the nature of the parent rock, climate, topography, and vegetation. A proper understanding of pedogenesis can only be obtained by quantitative mineralogical analysis of all stages from the parent material, through the weathering rock and subsoil layers to the most highly weathered surface horizons of the soil profiles. It is primarily with this kind of investigation in mind that the method described here has been evolved.

Apparatus and technique. A photographic technique is used with 9 cm. precision powder cameras having double-slit collimation, the slit dimensions being $4{\cdot}35 \times 0{\cdot}27$ mm. The design of the cameras is similar to that described by MacEwan (1949). Co-$K\alpha$ radiation was chosen as it is the most useful for soil minerals in general; it gives fairly large diffraction angles, an important consideration when dealing with large spacings,

and, unlike the commonly used Cu-$K\alpha$ radiation, it does not give fluorescent scattering with specimens containing iron. Although Co-$K\alpha$ X-rays are strongly absorbed by dense specimens this effect can be reduced to a negligible minimum by the specimen preparation technique described below. Ilford industrial 'B' X-ray films are used and exposure times are adjusted to give an ideal density maximum of about 0·5 units, although densities up to 0·8 can be used. Film processing conditions are carefully standardized.

The photometer is a Hilger non-recording X-ray microphotometer, which has been converted to a recording unit using a Kipp drum camera. The six-volt supply for the light source of the photometer is obtained from accumulators. The response of the photocell was checked, using Ilford neutral density filters to give a series of standard steps. As the density range varies from film to film the sensitivity of the photometer is adjusted for each run so as to use the full (12 cm.) width of the recording paper. At the end of each run the levels of at least two of the standard steps are recorded on the same chart at the same sensitivity setting, so that the density value can be found for any point on the curve. Fig. 1 shows the photometer tracing from a specimen containing aluminium and hematite in the weight ratio 1:2. The two standard steps have the density values 0·25 and 0·30.

Calibration films were obtained using a rotating lead step-sector, the blackness levels being recorded along with the series of standard steps on the same photometer charts. From these charts the film strip densities were found and plotted against a linear time of exposure scale. This calibration curve was chosen in preference to a logarithmic one as it is more accurate at low density levels. This is especially true for the soft Co-$K\alpha$ radiation, which is appreciably absorbed in the film base between the two emulsions and in the emulsions themselves, so that the inner emulsion layer reaches its critical density level before the outer, and the curve for the combined densities has two discontinuities. Another advantage of using low density levels is that exposure times are reduced. In practice, suitable densities are obtained by giving the same exposure as would be used to get photographs suitable for visual inspection on the faster Ilford 'G' films.

The cylindrical specimens have a diameter of 0·125 mm. and are prepared by rolling the sample, mixed with an internal standard and a little 'Durofix' adhesive as a binder, between two glass plates as described by MacEwan (1949). This small specimen of concentrated material still has appreciable absorption effects, but these are greatly

reduced when two parts by weight of powdered gum arabic are mixed with the sample before making the specimen. This dilution by a light amorphous material gives a low and almost constant absorption value to all specimens. Dilution with 66 % by weight of gum corresponds to about 80 % by volume (for samples with the specific gravity of quartz),

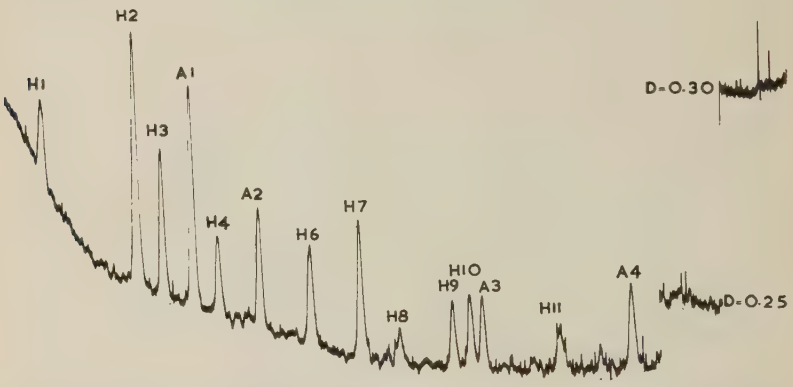

Fig. 1. Photometer record of the diffraction pattern from a mixture of hematite and aluminium in the weight-ratio 1:2. The peaks are numbered to correspond with table I.

and this large volume dilution has an incidental advantage in greatly reducing the amount of preferred orientation that occurs on making rolled specimens from samples containing platy or rod-shaped minerals. It is very important that the sample, the standard material, and the gum should be thoroughly mixed together and finely ground. Brindley (1945) considers theoretically the influence of particle size on the diffraction intensities from mixed powders, and shows that for any component it appears at a particle size depending on the absorption coefficient of that component, and that furthermore the effect of particle size on the relative intensities from two components is proportional to the difference between their absorption coefficients. Since the amount of sample material contained in the irradiated part of the specimen in this method is very small—about 0·2 mg.—results will be representative of the whole sample only if sampling errors are avoided.

Universal intensity scale. In order to make the method applicable to routine determinations, an arbitrary universal scale of intensity has been set up using potassium chloride as the primary internal standard. The value of the 200 reflection has been taken as 1000 and the other powder lines have been given corresponding values obtained from the

means of measurements from a number of films from different specimens prepared in the standard way (see table I). Using the same techniques with standard mixtures of potassium chloride and various pure minerals, the intensities of the diffraction lines of these minerals have been put on the same scale.

As potassium chloride is water soluble, very small amounts can be measured accurately by adding the required amount of a dilute solution of the chloride to the sample, which is then dried and reground. This method gives a very intimate mixture. A water-soluble standard, however, has the disadvantage that its particle size tends to increase by recrystallization in the presence of traces of moisture, giving spotty diffraction lines. After the final grinding it is therefore essential to keep the sample and specimen dry. It was found, for example, that when finely ground potassium chloride was added to air-dry montmorillonite spotty lines were obtained, but if the clay was dried at 300° C. before mixing with the salt, the diffraction pattern showed smooth lines. Another difficulty with potassium chloride is the possibility of chemical reactions occurring with the sample. For example, ammonium salts or ammonium-saturated clay minerals will react to give ammonium chloride at the expense of some of the potassium chloride. It was found experimentally that these and similar reactions may occur at room temperatures in the presence of hygroscopic moisture, or on heating oven-dry material to 500–600° C. Since heating to these temperatures is a standard treatment in the identification of some minerals it is important that any internal standard present should be unaffected, so that changes in the relative densities of the diffraction lines can be detected. In practice, therefore, potassium chloride is frequently not the most suitable material to use, but it is a convenient reference against which other possible standards can be calibrated. The actual choice of a standard for any particular determination may depend on a number of considerations such as the position and distribution of the diffraction lines, solubility in water or other liquids, chemical reactivity, hardness, or thermal stability.

The properties of corundum make it a convenient standard in many cases. It has been found useful in the determination of crystalline compounds in dried plant leaves, where its presence helped in the grinding of the soft material. It frequently happens that the amount of material available for analysis is small, and the ideal amount of internal standard necessary may be very small. For these cases a mixture of 10 % corundum in powdered gum arabic has been prepared, and small amounts

of corundum can be obtained by weighing out suitable amounts of the mixture. Powdered aluminium has also been used as a standard (Brindley and Ridley, 1938).

Most of the internal standards used belong to the cubic system, and have therefore the advantage of giving diffraction patterns with few and intense lines. This means that the chances of line coincidence with the patterns of other materials in mixtures are reduced, and also that, to give lines of suitable density, relatively small amounts of internal standard are necessary.

Table I gives the intensity scale values and interplanar spacings for a number of common minerals and possible standards. The figures are all based on peak-height measurements, which have been found reliable for all well crystallized materials of suitable particle size.

In theory, any two uncontaminated lines, one from the standard and one from the material to be determined, should be sufficient; but it is preferable to measure a few of the strong lines of each pattern. The amount of the unknown is found from the equation:

$$x = 100aI_sI_{xm}/sI_xI_{sm},$$

where x = percentage of unknown, s = weight of sample used, a = weight of internal standard added, I_x = universal scale intensity of line of unknown, I_{xm} = measured intensity of line of unknown, I_s = universal scale intensity of line of standard, and I_{sm} = measured intensity of line of standard.

The accuracy of the method is dependent on a number of variable factors: the number of components in the mixture, the absolute intensity of the diffraction patterns of the components, the level and uniformity of the film background, particle size and shape, &c. In simple mixtures minerals like quartz and hematite can be determined within about 5 % (table II). For minerals with variable chemical composition such as feldspars or chlorites in which the relative intensities of the powder lines vary, errors may arise through the use of the wrong intensity scale values. It may be possible, however, to use the measured intensity values to identify such minerals if data are available for a series of pure members of known composition. Fig. 2 shows the variation in intensity for the strongest line (3·17–3·23 Å.) of four plagioclase feldspars with composition.

For many purposes only an approximate estimate of the composition of mixtures is required and this can be obtained by visual inspection of films. The accuracy of such visual estimations can be greatly improved

TABLE I. Universal Intensity Scale.

	Potassium chloride		*Aluminium*		*Corundum**		*Quartz*		*Calcite*	
	d, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*
1	3·14	1000	2·33	870	3·47	145	4·26	150	3·86	55
2	2·22	655	2·03	430	2·55	225	3·34	895	3·04	695
3	1·82	210	1·43	270	2·38	105	2·46	90	2·49	85
4	1·57	95	1·22	290	2·08	240	2·28	70	2·28	140
5	1·40	230	1·17	90	1·74	130	2·23	40	2·10	120
6	1·28	155	1·01	55	1·60	275	2·12	50	1·91	185
7	1·11	45			1·51	15	1·98	35	1·87	165
8	1·05	110			1·40	80	1·82	130	1·60	65
9	0·99	85			1·37	155	1·67	45	1·52	50
10	0·95	75			1·24	40	1·54	110	1·44	50
11					1·19	15	1·37	115	1·18	35
12							1·26	40	1·15	45

	Hematite		*Goethite*		*Lepidocrocite*		*Gibbsite*		*Kaolinite*	
	d. Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*
1	3·67	145	4·96	80	6·25	660	4·83	620	7·15	120
2	2·69	540	4·17	450	3·28	420	4·35	120	4·45	50†
3	2·51	290	3·36	65	2·79	90	3·30	30	4·35	60†
4	2·20	150	2·68	265	2·47	245	2·45	60	4·17	60†
5	2·07	40	2·56	80	2·08	45	2·38	50	3·57	130
6	1·83	185	2·47	115	1·93	220	2·16	30	2·55	45
7	1·69	265	2·44	355	1·84	65	2·04	40	2·49	40
8	1·59	60	2·23	100	1·73	75	1·99	30	2·37	20
9	1·48	140	2·18	180	1·53	40	1·91	30	2·33	50
10	1·45	145	1·71	195	1·52	90	1·80	25	2·28	30
11	1·31	85	1·55	150	1·49	35	1·75	30	1·66	25
12	1·25	30	1·50	85	1·45	50	1·69	25	1·49	35

	Pennine		*Pennine* 600° *C.*		*Microcline*		*Oligoclase*		*Labradorite*	
	d, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*. Å.	*I*
1	14·5	75	14·2	250	4·22	70	4·19	110	4·05	135
2	7·14	135	7·10	25	3·99	35	3·87	75	3·88	25
3	4·78	105	3·54	25	3·76	40	3·77	115	3·77	120
4	4·60	30	2·81	60	3·68	35	3·20	530	3·66	85
5	3·58	105	2·67	30	3·49	75	2·99	50	3·37	60
6	2·86	35	2·60	15	3·37	65	2·93	115	3·20	480
7	2·59	45	2·55	15	3·25	320	2·85	55	3·01	55
8	2·55	70	2·45	50	3·03	50	2·55	40	2·94	95
9	2·45	50	2·24	20	2·96	90	2·10	35	2.84	50
10	2·38	25	1·88	10	2·91	85	1·83	60	2·53	90
11	1·58	30	1·71	10	2·16	60	1·80	60	1·83	50
12	1·54	65	1·54	30	1·80	65	1·78	55	1·77	60

* These corundum intensities may be too low as the material was prepared by igniting synthetic gibbsite, and complete recrystallization may not have occurred.

† Doubtful values from broad overlapping lines.

if the true relative intensities of the powder lines are known. In general it is usually simple to decide by visual observation whether one powder line on a photograph is stronger or weaker than another, but it is very difficult to say by how much. When the two lines compared have equal intensities the term I_{xm}/I_{sm} in the above equation becomes unity and the

TABLE II. Analysis of synthetic mixtures using aluminium as internal standard, from means of measurements of lines on both sides of one film for each mixture.

	Quartz.	*Hematite.*	*Goethite.*
Weight % in mixtures	33·33	33·33	50·00
Number of powder lines used	5	6	6
Means of determinations %	36·9	34·8	53·2
Standard deviation	1·7	2·1	3·7

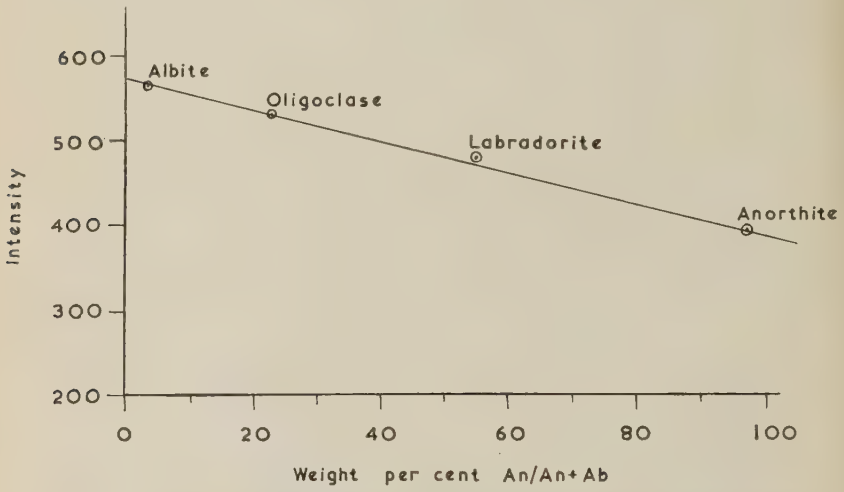

FIG. 2. The variation with composition of the intensities of the strongest lines (3·17 to 3·23 Å.) of plagioclase feldspars.

amount of the unknown can be calculated directly from the universal scale figures. For example, if the amount of quartz in a sample is to be estimated, a mixture can be made of two parts of sample to one of corundum along with six parts of gum arabic. Then, in the powder photograph of a specimen prepared by the standard procedure, by comparing the third corundum line with the third quartz line (as numbered in table I) one can tell if the amount of quartz is greater or less than $(50 \times 105)/90 = 58\ \%$. Similarly, by comparing the first quartz line with the first corundum line, and the eighth quartz line with the eighth corundum line, values are obtained above or below 48 % or 31 % respectively. There is a danger in the visual method that coincident lines may unwittingly be used, but these can readily be detected on photometer curves as they will give relatively high values compared with the other lines of the same component.

The relative intensities of the diffraction lines of single compounds found by the method described here are consistent with the counter data

in the American Society for Testing Materials powder diffraction data cards. Hanawalt, Rinn, and Frevel (1938) also obtained values similar to more recent counter data. Their intensities were obtained by visual comparison of the lines with a series of calibration film strips; and Mo-$K\alpha$ radiation was used so that absorption effects would be small.

The method described here has been widely applied to analyses of clay, silt and sand fractions of soils, rock and mineral specimens, fertilizers, &c., and universal scale intensity data are gradually accumulating. If a universal intensity scale could be generally adopted in the publication of X-ray powder diffraction data, it would be possible to use such information for approximate quantitative analysis, without the necessity of obtaining pure samples and preparing special calibration mixtures.

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SHORT COMMUNICATIONS

p-Veatchite from Yorkshire.

Clark *et al.* (1958 and 1959) have established that veatchite ($SrO.3B_2O_3.2H_2O$) is monoclinic and belongs to the space-group $A2/a$ or, less likely, Aa. Braitsch (1959) has recorded a new mineral, whose properties and powder photograph are almost identical with those of veatchite, but which belongs to the space-group $P2_1/m$ or $P2_1$. Since spectrographic work showed that boron and strontium were the principal constituents of this mineral, Braitsch assumed its chemical identity with veatchite and named the new mineral *p*-veatchite.

A mineral from the Permian lower evaporite bed of the Eskdale No. 2 boring in Yorkshire was described as veatchite by Stewart, Chalmers, and Phillips (1954), with a chemical analysis which agreed with the formula $SrO.3B_2O_3.2H_2O$. Single-crystal X-ray work now proves that this mineral is *p*-veatchite, and the identity of chemical composition of the two minerals is therefore confirmed. The data for the Eskdale mineral are as follows: a 6·74 ± 0·02 Å., b 20·62 ± 0·05 Å., c 6·63 ± 0·02 Å., β 119° 38′ ± 15′. Space-group $P2_1/m$ or $P2_1$. Cell volume, 797 Å^3. The presence of a centre of symmetry is suggested by the fact that a negative result was given for the Giebe and Scheibe test for piezoelectricity. These data show close agreement with those of Braitsch, although β is slightly greater.

The only two examples of *p*-veatchite so far described occur in evaporites of marine origin. The German material was found in water-insoluble residues from the Zechstein 'Ältere Steinsalz' below the Stassfürt Potash Zone, in the potash mine Königshall-Hindenburg, Reyershausen. Its associates are halite and anhydrite, with small quantities of clay, boracite, pyrite, quartz, and magnesite. The Yorkshire mineral has the same associates, with the exception of boracite. Veatchite, on the other hand, has been found in Californian localities associated with colemanite and howlite, partly in veins cutting limestone.

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F. H. Stewart

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BOOK REVIEWS

Répertoire de Matériel Cristallographique. Edited by A. J. Rose. xxvi+126 pp. Paris: the Apparatus Commission of the International Union of Crystallography. 2nd edn, 1959. Price fr. 12.50; $2.50 (incl. postage).

This is a second, greatly enlarged edition of the *Index of Manufacturers of Apparatus and Materials Used in Crystallography* first published in 1956. It tabulates equipment and services (with the names of suppliers), published crystallographic charts, nets, and tables, and textbooks. This matter should be very useful, and is well indexed. But a list of journals that include the words 'mineralogy' or 'crystallography' in their titles is almost valueless, for it omits journals, such as Journ. Amer. Chem. Soc., that lack the keywords in their titles but often publish material of crystallographic interest, while including several journals of very minor importance. Nor are 23 pages of advertisements by manufacturers of much value, since they duplicate information already listed. Despite its failings, the work should be of value to crystallographers seeking sources of supply of apparatus and materials. No attempt has been made to assess the relative merits of the equipment listed. The text is in French, with indexes in French and English. Distribution will be free to crystallographers through the National Committees of countries adhering to the Union. Further copies may be purchased from the editor at 1 rue Victor-Cousin, Paris 5; remittances (with order) should be payable to 'Société française de Minéralogie et de Cristallographie (I. U. Cr.)'.

Von Hippel (Arthur R.). *Molecular Science and Molecular Engineering.* London (Chapman & Hall), New York (John Wiley & Sons Inc.), 1959, xv+446 pp. Price 148*s*.

Two previous volumes in this series, *Dielectrics and Waves* and *Dielectric Materials and Applications*, dealt with particular physical properties of materials and their practical applications. The theme of this

book is more general; it is the design of materials with prescribed properties. This contrasts with the mineralogist's study of the properties of naturally occurring substances and fundamentally, as the title shows, it is a subject for the chemist.

The principal contributor several times emphasizes the need for a broad unified outlook on a problem that needs, as authors, two dozen specialists in electro-physics, geophysics, combustion and explosives, physical chemistry, mechanical engineering, ferromagnetics, ferroelectrics, atomic energy, and acoustics. Any probable reader is likely to find some section that contains nothing new to him, though he may well profit from the general picture presented. Mineralogists will find chapters of special interest on crystals, their growth and physical properties, but should remember that the author's whole purpose is to get them looking farther.

After an account of classical concepts of electrical science and engineering, the book deals with structures of atoms and molecules. Electrical conduction and breakdown of gases, the electrical state of the atmosphere, and micro-wave breakdown lead to a discussion of gas discharges as technical devices. The formation of condensed systems is considered thermodynamically and from the structural viewpoint. These systems include condensation polymers. A good deal of attention is given to state of perfection of crystals, effects of irradiation on materials, plasticity, ferroelectrics, and ferromagnetics.

The last chapter on molecular engineering and air vehicles of the future, which touches on some of the possible applications of the ideas developed, might with advantage have been expanded; more detail would have been welcome. From the tables here it may be seen that although molecular engineers are driven to synthetics they still depend greatly on mineral resources.

H. M. P.

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